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PRODUCTION OF GASEOUS FUEL BY PYROLYSIS OF MUNICIPAL SOLID WASTE

By

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FINAL REPORT ON
CONTRACT NO. NAS 9-14305

To

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ABSTRACT

Contract No. NAS 9-14305 was awarded by the Urban Systems Project Office of the Johnson Space Center to the Resource Recovery Systems Division of the Barber-Colman Company to evaluate the quantity and quality of the fuel gas produced by an already-constructed solid waste pyrolysis system.

Pilot-plant tests were conducted on simulated solid waste. Typically, the feed was a mixture of 50% shredded newspaper, 5% wood waste, 3% polyethylene plastics, 10% crushed glass, 8% steel turnings and 24% water. In some tests, the feed contained 7% moisture.

All tests were conducted at 1400 °F in a lead-bath pyrolyser. Cold feed was deaerated by compression in a screw feeder. The compacted waste dropped onto a moving hearth of molten lead. Pyrolyzed waste is scraped off the end of the hearth by a paddle wheel and dropped into a screw conveyor which transports it to a sealed storage container.

The solids were retained for about one minute on the hearth. About 80 percent of the feed's organic content was converted to gaseous products--benzene, toluene, and a medium-quality (500 btu) fuel gas; 12 percent to water; and 8 percent remained as partially pyrolyzed char and tars. The gaseous products contain over 90 percent of the energy inherent in the incoming waste. A surplus is produced. Less than 50 percent of the energy available in the products must be used as fuel to sustain the system. Actual system efficiency ranges from 50 to 70 percent depending on the efficiency in utilizing the sensible heat of the flue gas (from the pyrolyzer's radiant heaters).

Over 40 percent of the carbon in the feed is converted to benzene and toluene. In ten tests, benzene production exceeded 10 percent of the weight charged to the pyrolyser. At today's prices, this represents a potential credit of over \$25 per ton of solid waste.

Most metals and glass are not affected by the short exposure to the 1400 °F reducing atmosphere. Moreover, metal sorting is made easier, because the garbage, paint, grease and plastic insulation coatings are removed in pyrolysis. The burden that must be sorted is reduced by an order of magnitude. The system requires minimal preprocessing. Most sorting can be accomplished after pyrolysis. Excessive size reduction is not necessary.

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Chemical analysis of the numerous samples was directed by Mr. William J. Scott. Mrs. Norma B. Wilson and Mr. P. T. Brodowski performed many of the assays.

The lead-bath pyrolysis system was suggested by Dr. W. Martin Fassell, Vice President and Division Manager, RRS Division. Mr. T. H. Crane, J. P. Miller, L. S. Gordon and J. A. Geyer collaborated in aspects of the design. W. R. Gregord, B. E. Morelock, E. P. Reed, M. R. Heathcoat, J. L. Whitesell, and M. S. Bell have been instrumental in the maintenance and modification of the original system.

Mrs. Margaret L. Bradley typed the final report.

SECTION 1

INTRODUCTION

This is the final report of NASA Contract No. NAS 9-14305. It summarizes the results of investigations conducted between August 1974 and February 1975 by the Resource Recovery Systems (RRS) Division of the Barber-Colman Co. The contract was administered by the Lyndon B. Johnson Space Center (JSC), Houston, Texas. Mr. Richard C. Wadle and Mr. T. G. Reese served as the Technical Monitors.

The objective of the contract was to evaluate the RRS PURETEC[®] Pyrolysis System. Emphasis was placed on the production of fuel gas from municipal solid waste.

1.1 ADVANTAGES OF PYROLYSIS

Pyrolysis, heating in the absence of air, promises

- o Volume and weight reductions of wastes for ultimate disposal.
- o Minimal air pollution problems, since air is not deliberately used in the process.
- o Recovery of the energy available from the waste in the form of a usable fuel.
- o Recovery of most of the metals in the wastes, and
- o Conversion of organic wastes to valuable chemicals or chemical feedstocks.

The PURETEC[®] System embodies the idea of floating the wastes on a moving stream of molten lead inside the furnace, thereby gaining several pronounced advantages:

- o Transport - As a transport mechanism, the lead stream is quite insensitive to the type and particle size of the wastes. Everything (except minute amounts of rare heavy metals) will float along in the stream, requiring minimum energy and few moving parts for transport.

- o Heat Transfer - With radiant tubes heating the wastes from above and the lead stream heating them from below, improved heat transfer results. Greater hearth loading and throughput are possible.
- o Metals Recovery - The molten lead accomplishes useful metals sorting. Common metals like aluminum, iron, and copper, having a limited solubility in molten lead, float on the surface, are cleaned off in transit, and recovered intact. The noble metals, tin, and zinc alloy with it and can be recovered periodically.

1.2 PROCESS EFFICACY

The PURETEC[®] Pyrolysis System is well suited for the disposal of municipal solid waste. Supporting pilot-plant tests are described in this report. The tests were performed on a simulated solid waste--a blend of newspaper, pine needles and bark, plastics, water, glass and metal turnings. In these tests, the solids were retained for about one minute at 1400 °F. About 80 percent of the feed's organic content was converted to a medium-quality (500 Btu) fuel gas; 12 percent to water; and 8 percent remained as partially pyrolyzed char and tars. The weight and volume were greatly reduced thus facilitating disposal.

The gaseous products contain over 90 percent of the energy inherent in the incoming waste. A surplus of gas is produced. Less than 40 percent of the gas must be used as fuel to sustain the system. Typically, the net efficiency of the system is about 60 percent for waste containing 25 percent moisture.

The molten-lead hearth is an effective heat-transfer agent. Rapid pyrolysis can be accomplished at relatively low temperatures. The gases can be flushed from the furnace and cooled quickly. The primary products of pyrolysis remain essentially uncracked.

Substantial quantities of aromatic compounds are formed. Over 40 percent of the carbon in the feed is converted to benzene and toluene. In ten tests, benzene production exceeded 10 percent of the weight charged to the pyrolyser. At today's prices, this represents a potential credit of over \$25 per ton of solid waste.

Most metals and glass are not affected by the short exposure to the 1400 °F reducing atmosphere. Moreover, metal sorting is made easier, because the garbage, paint, grease and plastic insulation coatings are removed in pyrolysis. The burden that must be sorted is reduced by an order of magnitude.

The PURETEC[®] System requires minimal preprocessing. Most sorting can be accomplished after pyrolysis. Excessive size reduction is not necessary.

1.3 PROGRAM RATIONALE

For the purposes of this program, attention was focused on the affect of major variables on system output. Those considered included

Feed-type, moisture content, particle size

Pyrolysis Time-Temperature History - solids, gases

In the interests of obtaining a uniform feed whose basic composition--organics, moisture, inerts--would approximate that of municipal solid waste, initial tests were conducted with commercial dried steer manure. This feed showed such variations from batch to batch, however, that it was decided to use a standardized, simulated solid waste made up of known percentages of purchased shredded paper wood waste, plastics, glass, and scrap metal, in accordance with national averages. Moisture content was varied.

The similarity of gas production with both feeds did indicate that the exact size and composition of the cellulosic wastes (the great majority of the organics) has little effect. It should be noted that the great majority of the organic wastes are thin in at least one dimension: paper, cardboard, cloth, plastics, leather, leaves, etc. We do not propose to design our system to completely pyrolyze an infinitesimal quantity of, say dowels, on the first pass. Rather, we will partially pyrolyze and embrittle organic chunks on the first pass; collect them automatically in the post-sorting process; regrind them (in a special small grinder, if useful); and recycle them through the furnace to extinction. Therefore, no particular tests involving particle size were conducted in this program.

The time-temperature history of the solids undergoing pyrolysis largely depend on furnace/hearth temperature, hearth loading, and retention time, as well, of course, as the moisture content of the wastes. The last three named were varied over ranges of interest. Furnace temperature proved to be so tightly constrained however, by upper limiting bounds (avoidance of slagging or glass melting above 1500 °F), and lower bounds (pyrolysis liquids, hydrogen hazards below 1325° F, and radiant heating efficiency) that the standard furnace temperature of 1400° F was used.

Insight into the effects of the time-temperature history of gaseous products was obtained by varying the gas takeoff point from the cooler feed end of furnace to the hotter back end.

The equipment, test methods and results are detailed in Section 2.

SECTION 2

EQUIPMENT, METHODS AND RESULTS

Pilot-plant tests were conducted on simulated solid waste. All tests were performed at 1400 °F. The principal intentionally varied parameters were the rate at which solid waste was added and its moisture content. Two blends of waste were investigated. One was formulated by mixing shredded newspaper, pine needles and bark, plastics, glass, metal turnings and water. In the other simulated waste, tissue pulp was used instead of newspaper. The feed rate was varied from about 25 to nearly 100 lbs/hr. The moisture content ranged from 7 to 40 percent.

The tests were conducted in a pilot plant consisting of the pyrolyser and all requisite supporting equipment except a dryer. In practice, the waste will be dried before pyrolysis. Drying will be accomplished by contacting the waste with the hot flue gases.

2.1 DESCRIPTION OF THE PYROLYSIS SYSTEM

The pilot-scale pyrolysis system is pictured in Figures 2-1 and 1a. Wastes enter the feed screw which by compression also deaerates and seals. The waste then drops into the furnace and onto a moving hearth of molten lead. When the pyrolyzed waste reaches the end of the hearth, the char is scraped off by a paddle wheel and dropped into the char screw which cools and deposits the solid residue in a sealed storage container.

The gases are taken off at the top of the furnace, quenched and scrubbed with water sprays. They then were flared after being sampled for subsequent analysis. In practice, of course, these fuel gases will be used to power the pyrolysis process; and the surplus can be used on or off site to generate heat and/or electricity for other uses. During this test and evaluation program, natural gas has been used to heat the furnace to avoid introducing extraneous variables in the gases from wastes.

The scrubber condenses moisture driven off the wastes in heating, together with water vapor formed from the wastes by chemical reactions during pyrolysis. This water plus entrained organics is the scrubber liquor which is recirculated for quenching and scrubbing purposes.

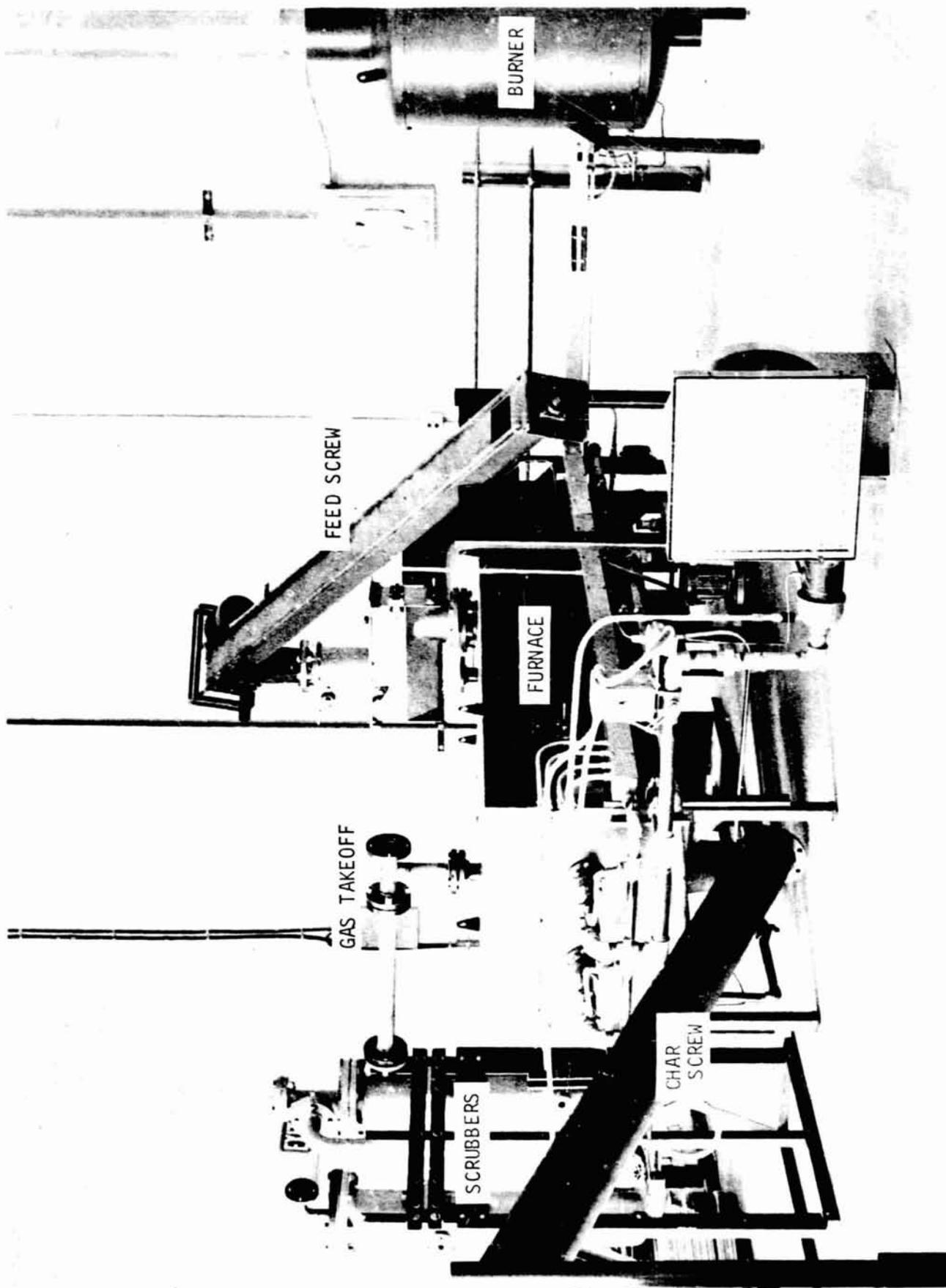


FIGURE 2-1 PURETEC® PYROLYSIS SYSTEM

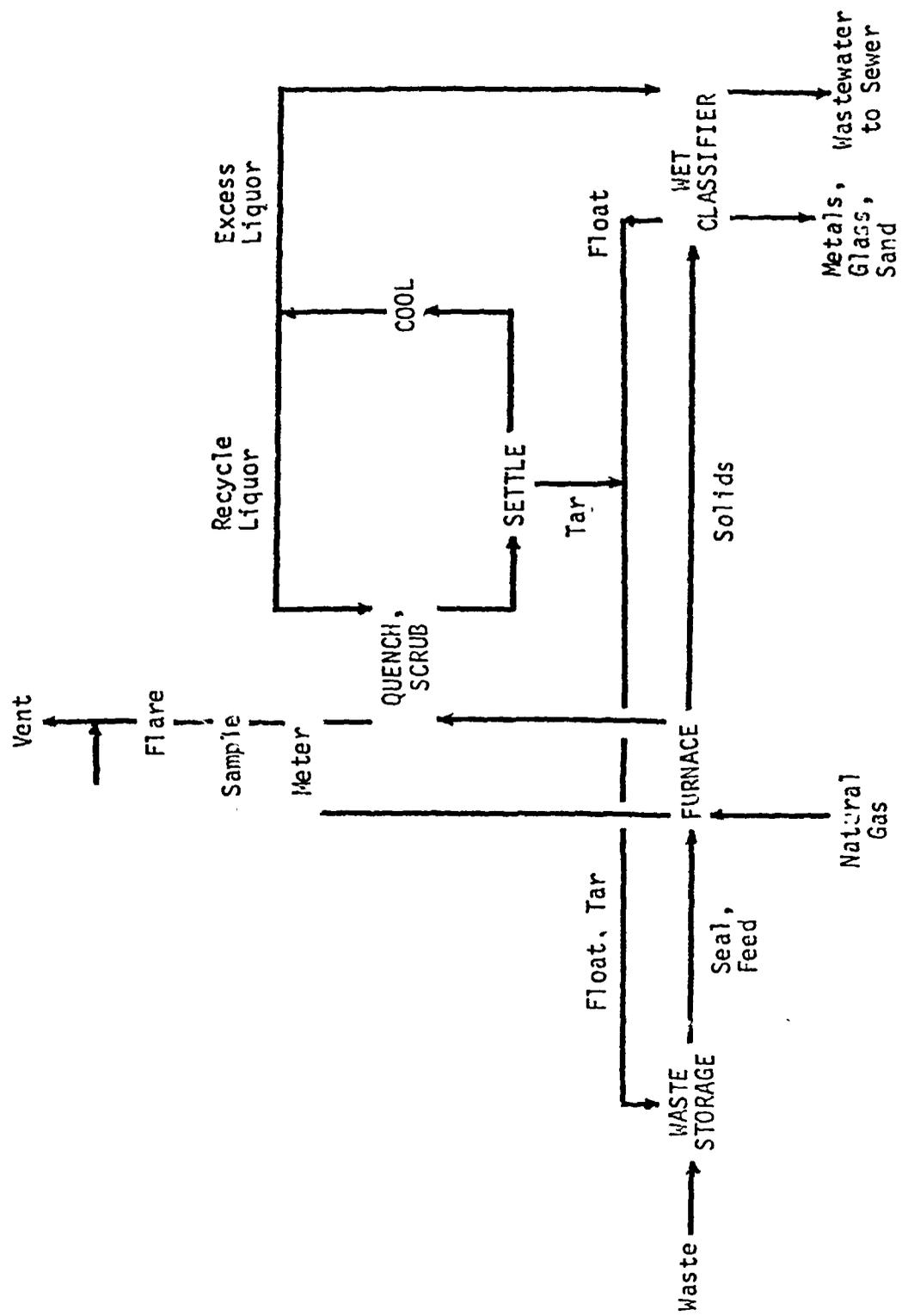


FIGURE 2-1a PYROLYSIS SYSTEM FLOW DIAGRAM

The scrubber also traps particulates swept out of the furnace by the gas, as well as oil mist and the condensate of the heavier vapors. Collectively these comprise the so-called residual tars and oils. They are entrained in the liquor.

2.2 SIMULATION OF SOLID WASTE

A simulated municipal solid waste was used, made up of known materials according to the recipe of Table 2-1, which approximates the average cited by others. (See, for example, E. R. Kaiser and S. B. Friedman, Combustion, May 1968, pp 31-36.)

TABLE 2-1 SIMULATED MUNICIPAL SOLID WASTE

<u>Constituent</u>	<u>Weight %</u>
Shredded Newspaper (dry basis)	50
Wood Wastes (dry basis)	5
Polyethylene Plastic	3
Crushed Glass	10
Steel Turnings	8
Water	24
	<hr/>
	100

Variations of this standard feed included

- o Reducing the moisture content to less than 10 percent to simulate the effects of partially drying the wastes with waste heat in the interests of system efficiency.
- o Increasing the moisture content to 40 percent to simulate the effects of adding sewage sludge.

2.3 SAMPLING AND OTHER METHODS OF MEASUREMENT

During each test, a portion of the gas flow was diverted intermittently from the furnace through a small outlet in the roof. The diverted gases were passed through a matting of fibrous glass and into a stainless-steel sampling bomb. The gases were assayed routinely by chromatography. Some samples were analyzed by mass spectroscopy. Particulate solids and tars were removed from the fibrous matting and assayed by proximate analysis.

The volume of gas samples was determined by measuring the flow into the bomb by a standard wet test meter. The volume of gas produced during an entire test was measured by a dry-displacement meter.

The weight of condensed liquors was estimated by measuring the increase in volume of circulating scrubber water. The concentration of organic substances in the scrubber water was monitored by analysis for chemical oxygen demand (COD).

Samples of the feed and char were assayed by proximate analysis. The major constituents comprising the tars and oils were identified by infrared

spectroscopy.

Entrained lead in the char was monitored by atomic absorption. Samples of the flue gas also were analyzed for lead by atomic absorption.

2.4 TEST RESULTS

Generally a test began at 0600. (The system had been heated to its operating temperature the previous day.) By 1000 the pyrolyser was again at temperature, and the feed system was initiated. At about 1630, the burners were turned off; and the system was secured. During the course of a test, measurements and samples were taken at various intervals. Sometimes the operating conditions were varied during the afternoon; and two tests were conducted in one day.

In following subsections, results are summarized first for pyrolysis of the baseline feed (waste containing 24% moisture). Data are presented for a feed rate of about 27 lbs/hr. Tests are summarized next in which the rate of feed was varied. Finally data are presented from tests conducted on feed containing different moisture contents.

2.4.1 PRODUCT YIELD UNDER BASELINE CONDITIONS

Table 2-2 presents a summary of data from Heat 021375. This test is typical of those performed under near mean conditions. That is to say, in this test the principal variables--rate of feed and moisture content--were at or near the median of the ranges investigated in the program. Specifically, the mean rate of feed was 27.5 lbs/hr; and the feed contained 24 percent moisture. The temperature was 1400 °F.

The mean yield of gas was 5.75 cu ft/lb feed.

In addition to the major constituents listed in Table 2-2, gases from the pyrolyser also generally contain the minor constituents listed in Table 2-3. Mass spectroscopy also has detected acetylene and propene in some samples of the pyrolysis gases.

In Appendix A, a mass balance is presented for Heat 021375. Figure 2-2 shows the nature of the yield in a graphical form. Over 75 percent by weight of the feed has been converted to gases and vapors--32% formed gas; 31% steam; and 14% benzene and toluene. Eighty percent of the remaining solids is inert glass and metal. The distribution is described in other terms in Appendix A. For example, about 42 percent of the feed carbon formed aromatic substances--mainly benzene and toluene.

TABLE 2-2
DATA SHEET, HEAT 021375

A. Composition of Gases and Vapors:

<u>Constituent</u>	<u>Percent By Vol.</u>	<u>Weight lbs/ft³ of gas</u>
Hydrogen	16.1	0.85×10^{-3}
Carbon Monoxide	26.0	19.3
Methane	21.6	9.14
Carbon Dioxide	20.4	23.8
Ethylene	3.2	2.42
Ethane	0.5	.39
Benzene	11.3	23.0
Toluene	.8	1.9
	<hr style="width: 50%; margin: 0 auto;"/> 99.9	<hr style="width: 50%; margin: 0 auto;"/> 80.80×10^{-3}

B. Total Volume of Gases and Vapors:

517 cu ft

C. Total Weight of Gases and Vapors:

$517 \text{ cu ft} \times 0.0808 \text{ lbs/ft}^3 = 41.9 \text{ lbs}$

D. Total Weight of Feed:

89.8 lbs

E. Total Weight of Condensed Liquor:

28.1 lbs

F. Total Weight of Scrubber Solids:

$27.8 \text{ grams in } 405 \text{ liters } (14.3 \text{ ft}^3) \text{ of gas};$
 $(27.8\text{g}/454\text{g/lb}) \times (517 \text{ ft}^3/14.3 \text{ ft}^3); \text{ or}$
 2.25 lbs

G. Proximate Analysis of Solids:

	<u>Moisture</u>	<u>Volatile Matter</u>	<u>Fixed Carbon</u>	<u>Ash</u>
Feed				
Sample A	27.07	49.72	7.12	16.08
B	29.41	49.34	6.20	15.04
Char	1.0	2.8	8.8	87.4

TABLE 2-2 (Continued)

H. Composition of Scrubber Solids:	
Tars and oils, principally naphthalene	45 percent
Carbonaceous char	45 percent
Fly ash	10 percent
I. Duration:	
4.62 hours	
3.33 hours at steady state	

TABLE 2-3

MINOR CONSTITUENTS DETECTED IN PYROLYSIS GAS BY MASS SPECTROSCOPY

<u>Constituent</u>	<u>Typical Amount, Percent By Volume</u>
Oxygen	0.003
Methylacetylene	.02
Propane	.08
Butadiene	.05
Cyclopentadiene	.03
Thiophene	.01
Styrene	.003
Xylene	.002

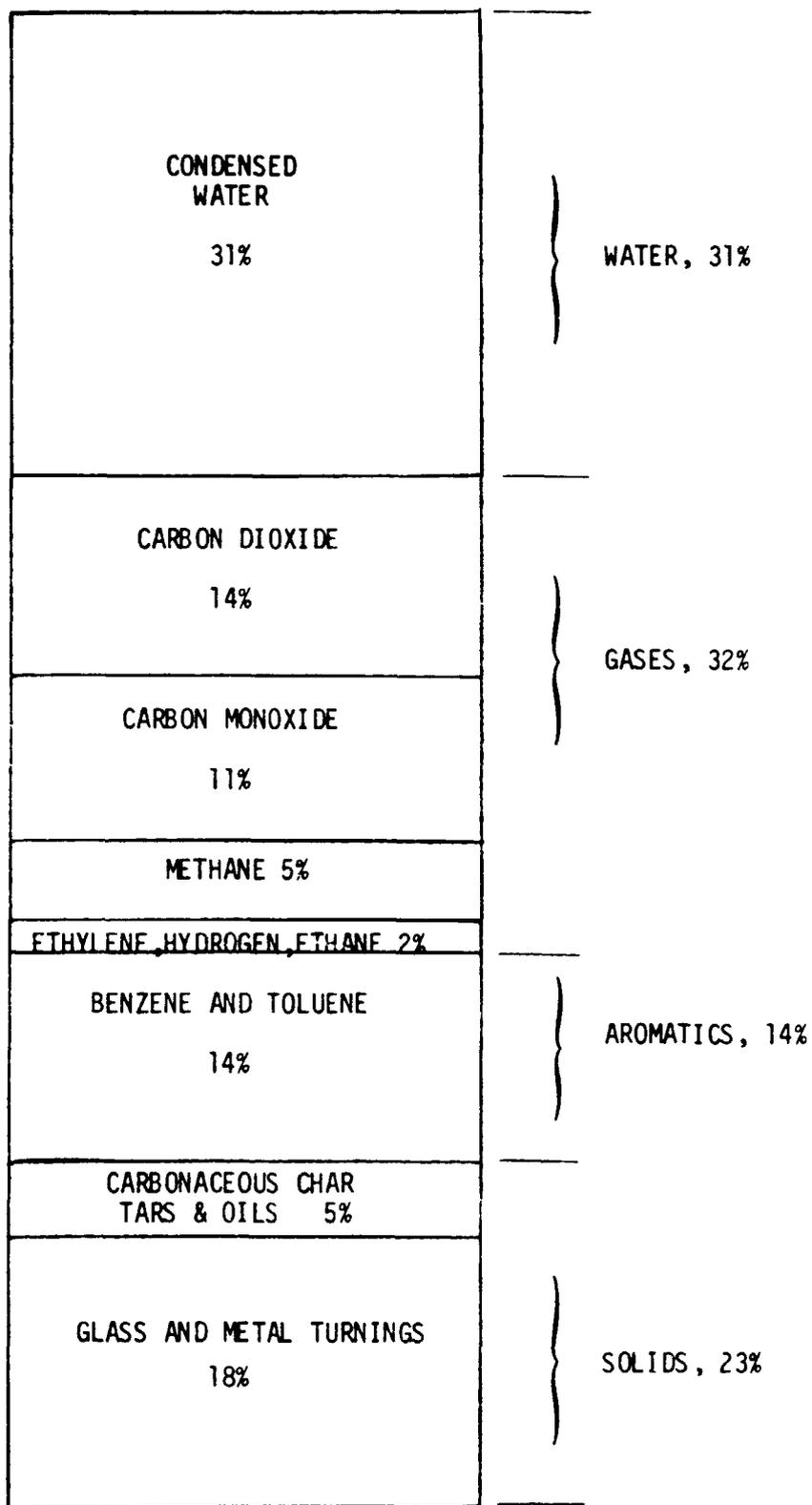


FIGURE 2-2 PRODUCTS FROM PYROLYSIS OF SIMULATED SOLID WASTE

2.4.2 EFFECT OF FEED RATE ON YIELD, BASELINE MOISTURE

A series of tests was conducted on feed containing 24-percent moisture in which the rate of feed was varied. The range was from less than 15 to more than 40 lbs/hr. Table 2-4 summarizes the results. Note that the means are in excellent agreement with the corresponding values recorded in Appendix A for Heat 021375, which was conducted under near mean conditions.

Perhaps significantly, the sum of the three combustion gases--hydrogen, carbon monoxide and carbon dioxide--is nearly invariant, as one can see from the summary of data presented in Table 2-5. See Section 3 for further discussion.

Viewed overall, the trends in the data from this series indicate that the yield of aromatic substances--benzene and toluene--is affected most significantly by varying the rate of feed. Increasing the feed rate increases the yield.

TABLE 2-5
VARIANCE IN SUM OF COMBUSTION GASES
(Tests On Feed With 24-Pct Moisture)

Rate of Feed, lbs/hr	Percent By Volume			Sum of Three Gases
	H ₂	CO	CO ₂	
14	11.4	32.1	19.3	62.8
23	15.1	26.0	25.6	67.7
29	15.5	22.9	20.6	59.0
42	14.3	25.4	16.4	56.1
Mean:				61.4
Coefficient of Variation, Pct of Means				8

TABLE 2-4

YIELD FROM TESTS ON FEED CONTAINING 24-PCT MOISTURE

AT DIFFERENT RATES OF FEED

Rate of Feed, lbs/hr	Gas Yield, cu ft/lb of feed	Chemical Composition of Gases Percent By Volume						C ₆ H ₆	C ₇ H ₈
		H ₂	CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆		
14	4.6	11.4	32.1	24.6	19.3	4.9	0.6	6.7	0.4
23	6.1	16.1	26.0	18.9	25.6	2.0	0.4	10.7	0.2
29	7.3	15.5	22.9	22.6	20.6	3.6	0.6	12.4	1.1
42	6.4	14.3	25.4	20.3	16.4	3.0	0.4	18.7	1.4
27	6.1	14.3	26.6	21.6	20.5	3.4	0.5	12.1	0.8
44	18	15	15	12	19	36	23	41	73

Means:

Coefficient of Variation, Pct of Mean

A second series of tests was conducted at feed rates above the baseline level. The results are summarized in Table 2-6. There are significant differences in the yields of hydrogen and ethylene in this series compared to the previous. The levels and trends in benzene, however, are similar in the two series. The total yield of gas also is comparable in both.

In the second series, a vacuum pump malfunctioned; and air leaked into the sample line during the majority of tests. Thus considerable nitrogen was detected in most samples.

In Table 2-7, the sums of the three combustion gases--hydrogen, carbon monoxide and carbon dioxide--are listed for the tests comprising this second series. The mean value is in excellent agreement with that from the first series--63.2 versus 61.4 percent; and the coefficient of variation is equally small--5 pct in the second series and 8 pct in the first.

TABLE 2-7
 VARIANCE IN SUM OF COMBUSTION GASES
 (Second Series On Feed With 24-Pct Moisture)

Heat No.	Rate of Feed, lbs/hr	Percent By Volume			Sum of Three Gases
		H ₂	CO	CO ₂	
011475	33	17.8	24.3	22.1	64.2
011575	35	27.6	15.9	23.1	66.6
		28.8	16.1	18.7	63.6
011675	37	23.3	20.7	17.5	61.5
		21.3	16.8	18.1	56.2
012075	53	14.0	28.8	20.3	63.1
		9.3	35.8	17.2	62.3
		10.0	32.9	20.4	63.3
Mean:					63.2
Coefficient of Variation, Pct of Mean					5

TABLE 2-6
GAS YIELD FROM TESTS ON FEED CONTAINING 24-PCT MOISTURE
(Second Series)

Heat No.	Rate of Feed, lbs/hr	Gas Yield, cu ft/lb of Feed	Percent By Volume							
			H ₂	CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₆ H ₆	N ₂
011475	33	6.6	17.8	24.3	16.8	22.1	3.4	0.4	13.5	1.7
011575	35	7.5	27.6 28.8	15.9 16.1	17.5 21.5	23.1 18.7	1.5 2.4	0.2 .4	8.8 11.5	5.3 .7
011675	37	5.2	23.3 21.3	20.7 16.8	25.3 23.6	17.5 18.1	3.5 2.1	.4 .3	8.5 16.8	0.9 1.0
012075	53	6.2	14.0 9.3 10.0	28.8 35.8 32.9	25.6 25.7 22.8	20.3 17.2 20.4	7.0 8.8 9.6	1.4 1.3 1.5	1.3 1.1 1.7	1.5 .8 1.2
020775	40	5.5	3.8 17.4	42.0 35.9	25.0 24.7	18.8 13.8	7.2 4.4	1.0 .6	2.3 3.7	--- ---

In the second series, in Heats 012075 and 0207 , the yield of benzene is significantly less than in the test of the first series at a comparable rate of feed. (See the test at 42 lbs/hr listed in Table 2-4, page 2-9.) Curiously, the yield in ethylene is significantly greater in the second series than in the first. The decrease in benzene appears to have been compensated by an increase in ethylene.

The yield in methane, on the other hand, is remarkably consistent in all tests comprising both series. The following statistics compare the two sets:

	<u>Mean Pct Methane</u>	<u>Coefficient of Variation, Pct of Mean</u>
First Series	21.6	12
Second Series	22.8	14

2.4.3 EFFECT OF REDUCED MOISTURE, DIFFERENT FEED RATES

In another series of tests, the moisture level of the feed was reduced from 24% to 7%. The same relative portions of dry components were used in the simulated solid waste as in previously described tests. Table 2-8 summarizes the results.

Significantly less benzene formed in these tests. The yield of benzene as well as the yield of ethylene increased with increasing rate of feed. As in the previous series, the yield of methane was constant and nearly the same as in the two series conducted on feed containing 24-pct moisture.

Table 2-9 lists the sum of the three combustion gases--hydrogen, carbon monoxide, and carbon dioxide. Again, as in previous series, the sum is essentially invariant; and the mean value is about the same as in previous tests.

The total yield of gas also is about the same as in the previous tests for comparable rates of feed.

2.4.4 EFFECT OF INCREASED MOISTURE

Tests were conducted on two types of feed containing excessive moisture. The first was the simulated solid waste described in all previous tests but laden with 30-pct moisture. The second was a simulated solid waste concocted with tissue pulp instead of newspaper. The tissue-pulp waste had a greater capacity for water than that formulated from newspaper. Feed containing tissue pulp assayed about 40-pct moisture.

Tissue pulp is essentially 100 pct chemical pulp; whereas newspaper is a mixture of 85 pct groundwooc pulp and 15 pct chemical pulp. Therefore, tissue pulp is nearly pure cellulose, but newspaper contains significant amounts of lignin and hemicellulose in addition to cellulose. (These

TABLE 2-8
 YIELD FROM TESTS ON FEED CONTAINING 7-PCT MOISTURE
 AT DIFFERENT RATES OF FEED

Rate of Feed, lbs/hr	Gas Yield, cu ft/lb of feed	H ₂	CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₆ H ₆	C ₇ H ₈
23	8.5	15.8	35.9	25.8	17.0	3.1	0.4	2.0	tr
30	6.2	21.6	29.5	26.2	17.8	2.7	0.4	1.3	0.4
33	6.0	17.4	35.1	25.2	15.8	3.8	0.5	2.0	0.2
62	2.4	7.3	37.7	26.7	12.7	5.3	0.7	8.9	0.8
		18.3	33.5	25.7	16.9	3.2	0.4	1.8	0.3
		16	10	2	6	17	13	23	47
		15.5	34.6	26.0	15.8	3.7	0.5	3.6	0.5
		40	10	2	14	17	28	101	65

Mean of First 3:
 Coefficient of Variation,
 First 3 tests,
 Pct of Mean

Mean of all 4:
 Coefficient of Variation,
 All 4 tests,
 Pct of Mean

TABLE 2-9

VARIANCE IN SUM OF COMBUSTION GASES
(Tests on Feed With 7-Pct Moisture)

Rate of Feed, <u>lbs/hr</u>	Percent By Volume			<u>Sum of Three Gases</u>
	<u>H₂</u>	<u>CO</u>	<u>CO₂</u>	
23	15.8	35.9	17.0	68.7
30	21.6	29.5	17.8	68.9
33	17.4	35.1	15.8	68.3
62	7.3	37.7	12.7	57.7
Mean of First 3:				68.6
Coefficient of				0.5
Variation,				
First 3 tests,				
Pct of Mean				
Mean of 4 tests:				65.9
Coefficient of				8
Variation,				
All 4 tests,				
Pct of Mean				

facts are discussed extensively in Appendix A.)

There was a substantial yield in benzene and toluene from both feeds. The results of the tests are presented in Table 2-10. Note that the yield of methane is less than in most other tests at a comparable rate of feed. The yield of methane is less in the test on tissue pulp than in the test on newspaper.

In Table 2-11, the variance in the sum of the three gases--hydrogen, carbon monoxide and carbon dioxide--is shown for the two feeds. Note that the test on tissue pulp resulted in a greater percentage of these three gases than in the test on newspaper or any other tests on newspaper previously presented.

2.4.5 FROTH FLOTATION OF CHAR

Miscellaneous char was composited from a number of tests. A 2-kilogram sample of the composite was placed in a Denver Equipment Co. (Sub-A) flotation machine. Approximately 8 liters of scrubber liquor were added to the flotation machine. The resulting pulp was conditioned by mixing it for 3 minutes at 1200 rpm. No flotation agents were added. No aeration was employed during the conditioning period after which the suction device was activated fully to cause maximum aeration. The carbonaceous debris rose to the surface in a stable, fairly dry froth which was skimmed off and dried for chemical analysis.

Table 2-12 summarizes the degree of separation obtained in the test. Nearly 74 percent of the fixed carbon concentrated in the floated portion; and nearly 90 percent of the lead was contained in the unfloated sands. The scrubber liquor had been used in a number of pyrolysis tests. Its COD was 16,700 mg/l O. At the end of the flotation test, its COD was 13,500 mg/l O. The initial pH was 5.1; the final pH was 5.8.

2.4.6 TREATMENT OF SCRUBBER LIQUOR BY ACTIVATED CARBON

Approximately 40 grams of activated charcoal (granulated 4 x 12; manufactured by Darco, Atlas Chemicals Industrial, Inc.) was added to 160 ml of scrubber liquor. The mixture was stirred in a 400-ml beaker for several hours after which the liquor was filtered from the carbon and assayed. The following is a summary of the results:

	<u>COD, mg/l O</u>	<u>pH</u>
Before Treatment	17,600	5.3
After Treatment	4,050	5.3

Over 75 percent of the organic matter--as measured by COD--has been removed from the liquor by carbon adsorption. The adsorbed substances are mainly entrained and soluble benzene.

TABLE 2-10
GAS YIELD FROM TESTS ON FEED CONTAINING EXCESSIVE MOISTURE

Type of Feed	Rate of Feed, lbs/hr	Gas Yield, cu ft/lb of Feed	Percent By Volume							
			H ₂	CO	CH ₄	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₆ H ₆	C ₇ H ₈
Newspaper (30% H ₂ O)	49	4.9	21.7	25.6	21.4	18.4	3.2	0.4	8.2	1.1
Tissue Pulp (40% H ₂ O)	56	5.9	24.4	25.4	17.7	23.4	2.7	0.3	5.7	0.4
			26.8	23.8	15.2	25.0	2.2	.3	6.2	.5

TABLE 2-11
VARIANCE IN SUM OF COMBUSTION GASES
(Tests on Feed With Excessive Moisture)

Type of Feed	Rate of Feed, lbs/hr	Percent By Volume			Sum of Three Gases
		H ₂	CO	CO ₂	
Newspaper (30% H ₂ O)	49	21.7	25.6	18.4	65.7
Tissue Pulp (40% H ₂ O)	56	24.4	25.4	23.4	73.2
		26.8	23.8	25.0	75.6

TABLE 2-12
FROTH FLOTATION OF PYROLYSIS CHAR
DATA SHEET

A. Chemical Analysis

<u>Component</u>	<u>Weight, gms</u>		<u>Chemical Composition, Pct</u>				
	<u>Total</u>	<u>Pct of Total</u>	<u>Moisture</u>	<u>Volatile Matter</u>	<u>Fixed Carbon</u>	<u>Ash</u>	<u>Lead</u>
Floated Portion (Char Concentrate)	380	19.9	0.4	8.4	43.3	48.0	0.9
Unfloated Portion (Sand)	1537	76.9	0.04	2.5	3.8	94.0	2.0
Middling	30	1.5					
Water-Soluble Portion		1.7					
		100.0					

B. Calculated Head

Lead: $380 \times 0.009 = 3.42\text{g Pb}$
 $1537 \times 0.02 = \underline{30.74}$
 34.16g Pb
 $(34.16/1947) \times 100\% = 1.75\% \text{ Pb}$

Fixed Carbon:
 $380 \times 0.433 = 164.54\text{g FC}$
 $1537 \times 0.038 = \underline{58.41}$
 222.95g FC
 $(22.95/1947) \times 100\% = 11.45\% \text{ FC}$

C. Ratio of Concentration

Lead:
 $(30.74/34.16) \times 100\% \approx 90\%$

Carbon:
 $(164.54/222.95) \times 100\% \approx 74\%$

2.5 EQUIPMENT PROBLEMS

Only two equipment problems of any consequence materialized during the course of the test program.

The degree of gasification of the organics and the volume of fuel gas produced proved to be somewhat higher than anticipated, with the result that the water quench/scrubber section overloaded at high waste loading rates. This problem was rectified simply by installing a scrubber of larger capacity.

The other problem, with the waste feed screw, was of a more basic nature, although not concerning the pyrolysis process per se. To prevent, on the one hand, the entrance of air into the furnace, with consequent partial combustion and degradation of the produced fuel gas, and, on the other hand, the leakage of pyrolysis gases into the atmosphere, it is necessary to seal the waste loading mechanism. In the interests of simplicity, it was intended to provide a compression seal by an interruption of the feed screw itself. While a simultaneous seal and feed was accomplished, the screw was prone to build up compression along its length and jam, despite several modifications. In future designs we will divorce the seal and transportation functions.

SECTION 3

DISCUSSION OF THE TEST RESULTS

The tests, which were described in Section 2, were conducted principally to gain insight into three aspects of lead-bath pyrolysis. The three areas of interest were (i) the nature and extent of gasification, (ii) the calorific value of the gases and vapors, and (iii) the system efficiency. In following subsections, each of these areas is discussed.

Elementary statistical methods--the determination of the mean and the coefficient of variation*--are used in the following discussion. These methods enable one to focus attention on parameters that varied significantly. That is to say, statistical analysis isolates certain parameters whose variance is excessive. In tests of the type described in this report, a coefficient of variation less than 20 percent of the mean is probably within normal experimental error. A CV greater than 30 percent may be indicative of variance caused by changing process conditions. In other words, a significant change occurred.

3.1 NATURE AND EXTENT OF GASIFICATION

Typically over 75 percent of the wet weight is converted to gases in the pyrolysis of solid waste. In terms of reacting organic substances, the percentage conversion is in excess of 90. See Appendix A, Table A-12, page A-10.

In following subsections, first the composition of the gases is discussed; and, then, the effect of processing on the amount of gasification is examined.

*The coefficient of variation (CV) is defined as follows:

$$CV = (s/\bar{x}) \times 100\%$$

where s is the standard deviation; and
 \bar{x} is the mean.

3.1.1 EFFECT OF PROCESS PARAMETERS ON GAS COMPOSITION

Tables 3-1 and 3-2 summarize the statistical analyses of all gas samples from tests on feed containing 24-pct moisture and 7-pct moisture, respectively. The trends are discussed in following subsections.

a. Combined Mole Percentage of Three Gases--H₂, CO and CO₂.

Several times in the presentation of data (in Section 2), attention was called to the relative invariance of the combined volume percentage of hydrogen, carbon monoxide and carbon dioxide. The properties of gases are such that volume percent is also mole percent. Consequently, in most tests comprising this investigation, every unit volume of gas contained the same total number of H₂, CO and CO₂ molecules. This is undoubtedly indicative that the same basic products are formed from the thermal decomposition of one constituent in all tests.

Note that the sum of these three gases was greatest in the tests performed on tissue pulp. (See Table 2-11, page 2-16.) As tissue pulp is essentially pure cellulose, whereas newspaper contains lignin as well as cellulose; one concludes that an increase in cellulose causes an increase in the sum of the three gases--H₂, CO and CO₂.

According to C. G. von Fredersdorff and M. A. Elliott (Chapter 20, pp 892-1022, in Chemistry of Coal Utilization, Supplementary Volume; H. H. Lowry, Editor; John Wiley & Sons, Inc., New York, 1963), there is conflicting evidence concerning the chemical kinetics of pyrolysis. Carbon monoxide and carbon dioxide may be both primary products. On the other hand, carbon dioxide may be formed from carbon monoxide by subsequent oxidation. "The reactions,



are so rapid that they proceed essentially to completion with respect to oxygen disappearance." The carbon gasification reactions,



"are never at equilibrium at exit conditions. Equilibrium in these reactions requires practically 100% steam decomposition, and negligible CO₂ content, at temperatures above 2000 °F and pressures from 1 to 20 atm." Reaction 3-4 is generally slower than Reaction 3-3. "The water-gas shift reaction,



is considered to be primarily a heterogeneous phenomenon which occurs on the fuel surface, with very little reaction in the gas phase. At low steam decompositions, this reaction is...never at equilibrium, and its

TABLE 3-1

STATISTICAL ANALYSIS OF GAS COMPOSITION--FEED CONTAINING 24-PCT MOISTURE

Mean, in Mole Percent, and Coefficient of Variation(CV), in Pct of Mean

No. of Tests	Rate of Feed, lbs/hr	Sum of H ₂ , CO, CO ₂		CH ₄	Sum of C ₂ H ₄ , C ₂ H ₆ , C ₆ H ₆ , C ₇ H ₈		Sum of C ₆ H ₆ , C ₇ H ₈		
		Mean	CV		Mean	CV	Mean	CV	
2	<27	65.2	5	21.8	19	13.0	4	9.0	30
7	27-37	61.9	6	21.3	15	16.8	15	12.1	24
6	>37	62.6	6	23.9	9	13.3	40	5.0†	148†

† The mean and CV of six tests. If one of the six, which is 10 to 20 times greater than the other five, is discarded, then the mean is 2 pct and the CV is 52 pct.

TABLE 3-2

STATISTICAL ANALYSIS OF GAS COMPOSITION--FEED CONTAINING 7-PCT MOISTURE

Mean, in Mole Percent, and Coefficient of Variation(CV), in Pct of Mean

No. of Tests	Rate of Feed, lbs/hr	Sum of H ₂ , CO, CO ₂		CH ₄	Sum of C ₂ H ₄ , C ₂ H ₆ , C ₆ H ₆ , C ₇ H ₈		Sum of C ₆ H ₆ , C ₇ H ₈		
		Mean	CV		Mean	CV	Mean	CV	
1	23	68.7	--	25.8	--	5.5	--	2.0	--
2	30-33	68.6	0.6	25.7	3	5.7	20	1.6	30
1	62	57.7	--	26.7	--	15.6	--	9.7	--

rapid approach to equilibrium...is thought to occur primarily by virtue of steam disappearance through reaction (3-3)."

From the foregoing facts, it is apparent that the invariance noted in the sum of the H₂, CO and CO₂ contents is the natural consequence of operating the pyrolyser at a fixed temperature (1400 °F) and essentially the same retention time (about one minute*).

b. Percentage Methane In The Gas

This also is essentially invariant, although the CV is somewhat greater for methane than for the combined sum of H₂, CO and CO₂. Moreover, there is no discernible trend in the yield of methane from the pyrolysis of waste containing the same level of moisture. A unit volume of gas contains just as much methane in a test at a slow rate of feed as in a test in which the rate was fast. The yield, however, is slightly greater from pyrolysis of feed containing 7-pct moisture than from pyrolysis of feed containing 24-pct moisture.

c. Combined Percentage of Ethane, Ethylene, Benzene and Toluene

As this percentage constitutes the remainder of the gas, it also is essentially invariant. In other words, since the sum of the three gases (H₂, CO, and CO₂) is invariant and there is little variance in the methane content, the percentage of the remaining gases is essentially the same in every test. This is a potentially valuable characteristic of the system, because it implies that the combined yield of olefins (ethylene) and aromatics (benzene and toluene) is essentially invariant. In other words, every unit volume of gas contained virtually the same amount of the most valuable chemical-feedstock materials.

d. Percentage of Aromatic Substances--Benzene and Toluene

The variance in this parameter is so great that it is obvious that the yield was affected by changes in the process conditions. In other words, the yield of benzene and toluene depended on the rate of feed and moisture content.

The yield in aromatic substances is enhanced by operating in the presence of steam. This can be achieved either by processing feed containing a high level of moisture or by feeding very rapidly as in the last test listed in Table 3-2. The literature is full of references which cite improvement in the yield of aromatics (and of olefins) by using steam to flush the pyrolyser. (See, for example, the treatises by F. Asinger: Paraffins, Pergamon Press, Oxford, 1968, 896 pp, and Mono-Olefins, Pergamon Press, Oxford, 1968, 1167 pp.)

* In the lead-bath pyrolyser, retention time is determined primarily by the rate of feed and the rate at which the drag chain is rotating. The retention time ranged from about 0.5 to 1.3 minutes.

3.1.2 EFFECT OF PROCESS PARAMETERS ON GAS YIELD

In Table 3-3, a statistical analysis of total gas yield is summarized. The variance in the yield of aromatic substances also is included.

There is no discernible trend in the total gas yield from tests on feed containing 24-pct moisture. From 5.4 to 6.5 cu ft of gas was formed in tests in which the rate of feed ranged from 14 to 53 lbs/hr.

There is, however, a definite trend in the treatment of feed containing 7-pct moisture, as is shown graphically in Figure 3-1.

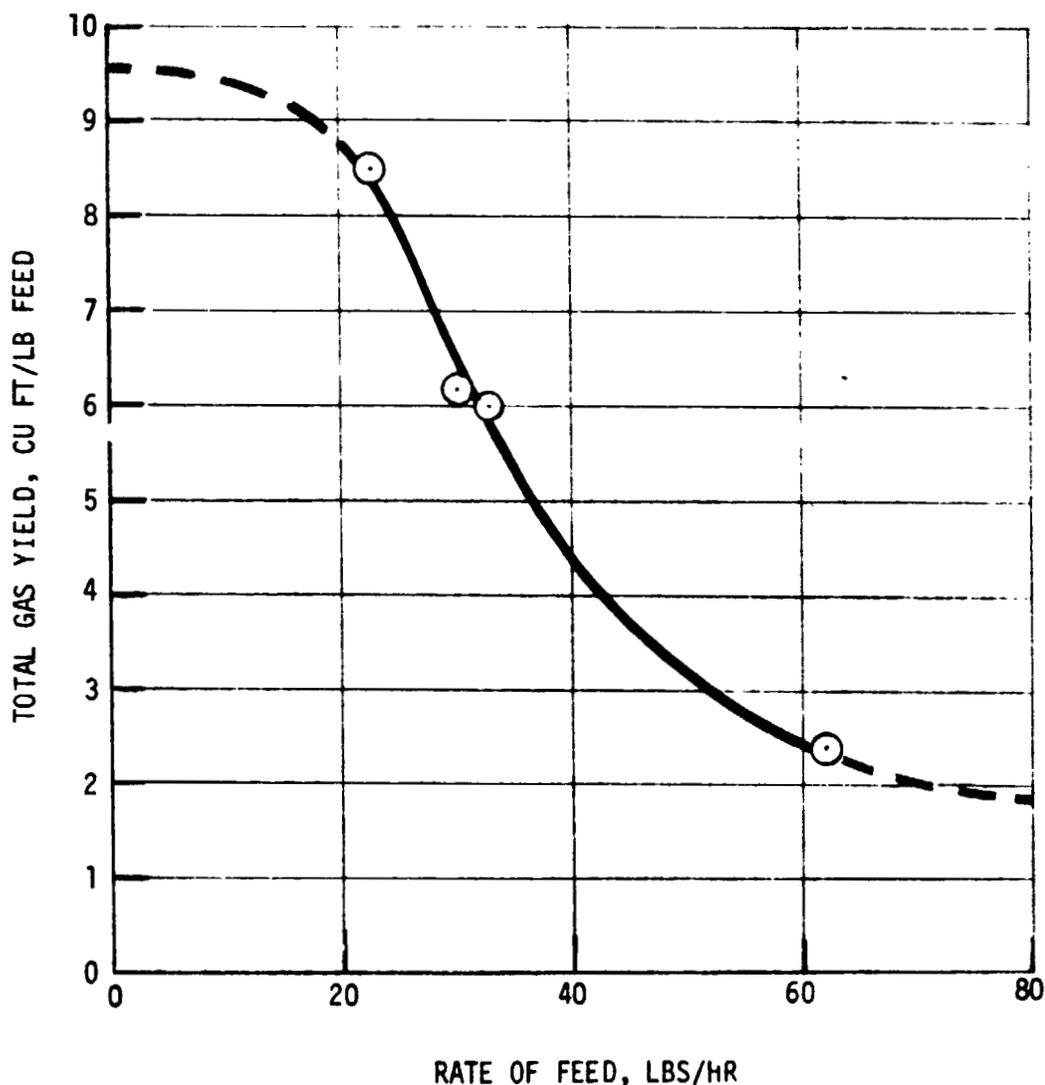


FIGURE 3-1. GAS YIELD FROM PYROLYSIS OF WASTE CONTAINING 7-PCT MOISTURE

TABLE 3-3

STATISTICAL ANALYSIS OF GAS YIELD

Percent Moisture	Rate of Feed, lbs/hr	Total Yield of Gas			Yield of Aromatics		
		cu ft/lb feed	Mean	CV†	cu ft/lb feed	Mean	CV†
30	49	4.9	--	--	0.5	--	--
24	14	4.6	5.4	20	0.3	0.5	57
	23	6.1			0.7		
	27	5.8	6.5	15	0.7	0.8	16
	29	7.3			1.0		
	33	6.6			0.9		
	35	7.5			0.8		
	37	5.2			0.7		
	40	5.5			6.0		
42	6.4	1.3					
53	6.2	0.1					
7	23	8.5	--	--	0.2	--	--
	30	6.2	6.1	2	0.1	0.1	--
	33	6.0			0.1		
	62	2.4	--	--	0.2	--	--

† Coefficient of Variation (CV) is expressed as percent of the mean

†† If the value from the test at 42 lbs/hr is discarded, the mean is 0.15 cu ft/lb feed and the CV is 47 percent.

The behavior illustrated in Figure 3-1 is in accordance with the basic considerations of heat transfer and combined mass and energy balance in a progressively thickening bed of waste. At small feed rates, the waste is pyrolyzed rapidly and completely. There is relatively little residual material on the hearth. As the rate of loading is increased slightly, the added waste too is pyrolyzed rapidly and completely. (This gives rise to the region of constant gas-production shown ideally between feed rates from 0 to about 10 lbs/hr in Figure 3-1.) As the rate of feed is increased above 15 lbs/hr, however; partially pyrolysed material and char begin to accumulate and form a bed on the hearth. Entering waste drops onto this bed. As the rate of feed increases, the height of the bed increases. Eventually only the top and bottom of the bed are pyrolyzed completely. The center or core is heated more slowly; and the extreme center may not pyrolyze completely in the retention time provided. (These phenomena result in the steadily declining segment of the curve.) At extremely rapid rates of feed, the heat input to the system becomes the limiting factor; and only a fixed thickness at the top and one at the bottom of the bed undergo pyrolysis. (The total gas yield approaches a constant value, but the yield per pound continues to decline as shown in the extreme right-hand portion of Figure 3-1.)

The explanation of Figure 3-1 given in the last paragraph is only partially correct. In addition to the effects caused by heat transfer through a bed of increasing thickness, there also is superimposed the effect of a gradually changing chemical composition of the gas as the rate of feed decreases or increases. For example, consider a baseline condition, that is, one at a feed rate of about 27 lbs/hr. Heat 021375, which is described in detail in Appendix A, is representative of this baseline.

If all of the char and scrubber solids had pyrolyzed and formed more of the same gas mixture (as formed in Heat 021375), then the gas yield would have been $5.75 \text{ ft}^3 \times (0.876/0.787)$ or 6.4 cu ft. The foregoing calculation indicates that the gas yield observed in tests at reduced feed rate can not be explained by merely postulating complete pyrolysis. One also must assume some shift in the gas makeup, i.e., heavy gases must be converted to light gases. For example, from the specific volumes listed in Table 3-4, it can be seen that the conversion of the benzene (0.01 lbs in Heat 021375) to hydrogen (plus carbon) would yield an additional 1.9 cu ft of gas. This would result in a total yield of 8.3 cu ft/lb feed--essentially the yield observed in the test on 7-pct moisture feed at 23 lbs/hr listed in Table 3-3. The formation of additional hydrogen instead of benzene is one of the possible alternatives which would yield 9 cu ft of gas per lb feed. The other is the conversion of water to hydrogen.

If the feed contains sufficient moisture, the formation of steam can be great enough that the gases are flushed rather rapidly from the bed. Moreover, steam is an excellent heat-transfer media; and, as it rises from the bottom of the bed, it conducts heat into the core. Consequently, in the case of moist feed, as the data from the tests on waste containing 24-pct moisture indicate, there is much less difference in the yield of gases as the rate of feed is varied.

TABLE 3-4
SPECIFIC VOLUMES OF THE GASES AND VAPORS FORMED
IN PYROLYSIS OF SOLID WASTE

<u>COMPOUND</u>	<u>SPECIFIC VOLUME, ft³/lb</u>
Hydrogen	189
Methane	23.6
Carbon Monoxide	13.5
Ethylene	13.4
Ethane	12.4
Carbon Dioxide	8.6
Benzene	4.8
Toluene	4.1

3.2 FUEL VALUE OF THE GASES AND VAPORS

A practical waste-disposal system should generate at least enough energy to sustain itself. Pyrolysis has the potential of producing surplus energy. In following subsections, tables are presented in which the fuel value is listed for the gases and vapors formed in the various tests comprising this investigation. The degree of self-sufficiency is estimated in Section 3.3.

In computing the fuel value of the gases and vapors from pyrolysis, the high heat values (HHV) (listed in Table 9-8, page 9-6, of the Chemical Engineers' Handbook, Fifth Edition, McGraw-Hill Book Co., New York, 1973) were used. These values are listed below:

<u>Compound</u>	<u>High Heating Value (HHV), Btu/cu ft</u>
Hydrogen	325
Carbon Monoxide	322
Methane	1013
Ethane	1792
Ethylene	1614
Benzene	3751
Toluene	4484

3.2.1 USEFUL ENERGY IN GASES AND VAPORS FROM PYROLYSIS OF WASTE CONTAINING 24-PCT MOISTURE

Table 3-5 lists the calculated fuel value for all tests on feed containing 24-pct moisture. In presenting the information, the calorific value of the gases has been tabulated separately as well as the energy obtainable from combustion of the combined gases and vapors. In Appendix B, computations are presented which indicate that the fuel content of the gases alone is generally sufficient to sustain the system. The vapors constitute the surplus fuel. Alternatively, the condensed vapors can be utilized as chemical feedstock.

A perusal of Table 3-5 reveals that the data are very consistent. The trends are delineated more clearly in the summary of the statistical analysis presented in Table 3-6. The total energy gained from a pound of feed increases as the rate of feed is increased--provided the rate of feed does not exceed 37 lbs/hr. At feed rates greater than 37 lbs/hr, the yield of benzene and toluene diminishes; and the contribution of these vapors to the total fuel value decreases. As benzene and toluene are much more energetic than any of the gaseous constituents, the total fuel value of gases plus vapors also diminishes. For the 9 tests in which the feed rate was 37 lbs/hr or less, the mean contribution of the vapors to the total fuel is 51 percent. (The CV is 16 percent.)

Of the various gaseous products, methane is the greatest single contributor to the fuel value. For the 15 tests listed in Table 3-5, the mean contribution of methane is 51 percent of the total fuel value of the gases. (The CV is 9 percent.)

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TABLE 3-5

FUEL VALUE OF GASES AND VAPORS FROM PYROLYSIS OF SOLID WASTE FEED CONTAINING 24-PCT MOISTURE

Rate of Feed, lbs/hr	Total Yield Gases & Vapors cu ft/lb feed	H ₂	CO	CH ₄	Btu/lb feed			C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₆ H ₆	C ₇ H ₈	Gas Only Btu/lb feed		Gas + Vapor Btu/lb feed		Btu/cu ft	
					CO	CH ₄	C ₂ H ₆						C ₃ H ₈	C ₄ H ₁₀	C ₆ H ₆	C ₇ H ₈	Gas Only	Gas + Vapor
14	4.6	170	475	1146	364	49	1156	83	2205	3444	479	749	416	875	416	875	416	875
23	6.1	319	511	1168	197	44	2448	55	2238	4741	367	777	416	875	416	875	416	875
27	5.8	303	486	1269	300	52	2458	206	2410	5076	416	875	416	875	416	875	416	875
29	7.3	368	538	1671	424	78	3395	360	3080	6835	422	936	416	875	416	875	416	875
33	6.6	382	516	1123	362	47	3342	---	2431	5773	368	875	416	875	416	875	416	875
35	7.5	673	384	1330	182	27	2476	---	2595	5070	346	676	416	875	416	875	416	875
		702	389	1633	290	54	3235	---	3069	6304	409	841	416	875	416	875	416	875
37	5.2	394	347	1333	294	37	1658	---	2404	4062	462	781	416	875	416	875	416	875
		360	281	1243	176	28	3278	---	2089	5366	402	1032	416	875	416	875	416	875
40	5.5	68	744	1393	639	99	474	---	2942	3417	535	621	416	875	416	875	416	875
		311	636	1348	391	59	763	---	2745	3508	499	638	416	875	416	875	416	875
42	6.4	297	523	1316	310	46	4489	402	2493	7384	390	1154	416	875	416	875	416	875
53	6.2	282	575	1608	700	156	302	---	3321	3623	536	584	416	875	416	875	416	875
		187	715	1614	881	144	256	---	3541	3797	571	612	416	875	416	875	416	875
		202	657	1432	961	167	395	---	3418	3813	551	615	416	875	416	875	416	875

TABLE 3-6
 SUMMARY OF STATISTICAL ANALYSIS--FUEL VALUE OF GASES AND VAPORS
 FROM PYROLYSIS OF FEED CONTAINING 24-PCT MOISTURE

No. of Tests	Rate of Feed, lbs/hr	Btu/lb feed		Gas + Vapor		Btu/cu ft			
		Gas Only Mean	CV	Gas Only Mean	CV	Gas + Vapor Mean	CV		
2	<27	2222	1	4092	22	423	19	763	3
7	27-37	2583	14	5498	17	404	9	859	13
6	>37	3077	13	4257+	36+	514	13	704++	31++

+ If the highest value, which is twice any other, is discarded, the mean of the remaining five is 3632 Btu/lb feed and the coefficient of variation is 5 percent of the mean.

++ If the highest value, which is nearly twice any other, is discarded, the mean of the remaining five is 614 Btu/cu ft and the coefficient of variation is 3 percent of the mean.

The energy content of the fuel gas, i.e., its value in Btu/cu ft, is greatest at feed rates above 37 lbs/hr; probably because benzene and toluene have been degraded to gaseous substances.

3.2.2 USEFUL ENERGY IN GASES AND VAPORS FROM PYROLYSIS OF WASTE CONTAINING 7-PCT MOISTURE

Table 3-7 summarizes the fuel value for the gases and vapors from the four tests on 7-pct moisture feed. Again methane contributes over half of the gaseous fuel value. (The mean contribution for the 4 tests is 54 pct; the CV is 2 pct.) For the three tests in which the feed rate ranged from 23 to 33 lbs/hr, the gases contributed 87 percent to the total fuel value. (The CV is 2 pct.)

Less fuel value was extracted from a pound of feed in these tests than in otherwise comparable tests on feed containing 24-pct moisture. The fuel gas, on the other hand, was richer--it ranged from 481-514 Btu/cu ft; whereas, in the tests on feed containing 24-pct moisture (and feed rates of 37 lbs/hr or less), the range is 346-479 Btu/cu ft.

3.3 SYSTEM EFFICIENCY

If solid waste containing 24-pct moisture were treated in a system arranged in the same manner as the pilot plant described in Section 2.1, the system efficiency would be 50 percent. In other words, only half of the energy available in the products would have to be burned to sustain the system. Detailed calculation of the system efficiency is presented in Appendix B.

The gases formed in pyrolysis are sufficient to sustain the system. The aromatic substances, benzene and toluene, can be marketed as chemicals or used elsewhere as fuel. This is an especially attractive characteristic of the lead-bath pyrolyser, because benzene and toluene are liquids which can be stored easily and transported conveniently. Many pyrolysis systems produce excess gas which is much less convenient to store or transport. These gases can be converted to liquids (such as methanol and polymer gasoline) only at additional expense.

The efficiency of the system can be increased to over 70 percent by using the sensible heat of the flue gases (the exhaust gases from the radiant heaters in the pyrolyzer) to evaporate a portion of the moisture in the feed. Supporting calculations are presented in Appendix B, Section B.6. In this version of the process, only a portion of the gas is needed to sustain the system. About 40 percent of the gases (and all of the benzene and toluene) are available for use elsewhere. As these gases have a fuel value of from 400 to 500 Btu/cu ft, they can be used readily in a conventional burner, internal combustion engine or electrical generator.

TABLE 3-7
FUEL VALUE OF GASES AND VAPORS FROM PYROLYSIS OF 7-PCT MOISTURE FEED

Rate of Feed, lbs/hr	Total Yield Gases & Vapors cu ft/lb feed	H ₂	CO	CH ₄	Btu/lb feed		C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₄ H ₆	C ₇ H ₈	Gas Only Btu/lb feed		Gas + Vapor Btu/lb feed		Btu/cu ft		
					CH ₄	C ₂ H ₄						Gas Only	Gas + Vapor	Gas Only	Gas + Vapor			
23	8.5	436	983	2222	425	61	638	---	4127	4764	486	560	481	548	488	572	514	883
30	6.2	435	589	1646	270	44	302	111	2984	3398	481	548	481	548	488	572	514	883
33	6.0	339	678	1544	368	54	450	54	2929	3433	488	572	488	572	488	572	514	883
62	2.4	57	291	649	205	30	801	86	1233	2120	514	883	514	883	514	883	514	883

SECTION 4

PROTOTYPE PLANT SIZE

As the concluding task of the program, the Contractor was directed to "perform cost-effectiveness studies utilizing the performance data from (the experiments conducted in the program)...together with cost-type data collected/generated (during the program)...to arrive at a recommended Prototype Plant size(s)." The results of this task are presented in this section. The layout of a modular unit is described, followed by a description of the full-scale process, and lastly a summary of its cost effectiveness.

4.1 MODULAR LAYOUT

Based on discussions with public officials, consulting engineers and others in the field of solid-waste management, we conclude that a system capable of processing 200 tons daily is an optimum module for municipal solid-waste disposal.

A single 200-TD module is sufficient to serve a city of 80,000. Plants servicing larger populations are best equipped with additional modules rather than a single larger unit. Plants larger than 1000TD generally are viewed as impractical, because the costs of collection over a very large area and transportation to a common site exceed the efficiencies gained in centralizing disposal. Consequently, we envision that disposal plants will utilize from one to five 200-TD modules. Equipped in this manner, a plant can sustain nearly full production, even when one module is temporarily down for maintenance. Moreover, one module can be shut down during periods of reduced load and reactivated at will.

The layout of a 200-TD pyrolyser and its ancillary equipment is shown in Figure 4-1. A plot, 220 feet by 160 feet, is required. The tallest structures are 40 feet high. In addition to the directly occupied area (0.64 acres), peripheral approaches are needed to assure access by trucks. The total area including driveways for the trucks is estimated to be 0.81 acres.

The system is self-sufficient. Enough gas is produced to supply its thermal and electrical needs. See Section 3.3 for a discussion of system efficiency.

There are three effluent streams from the system. They are the flue gases,

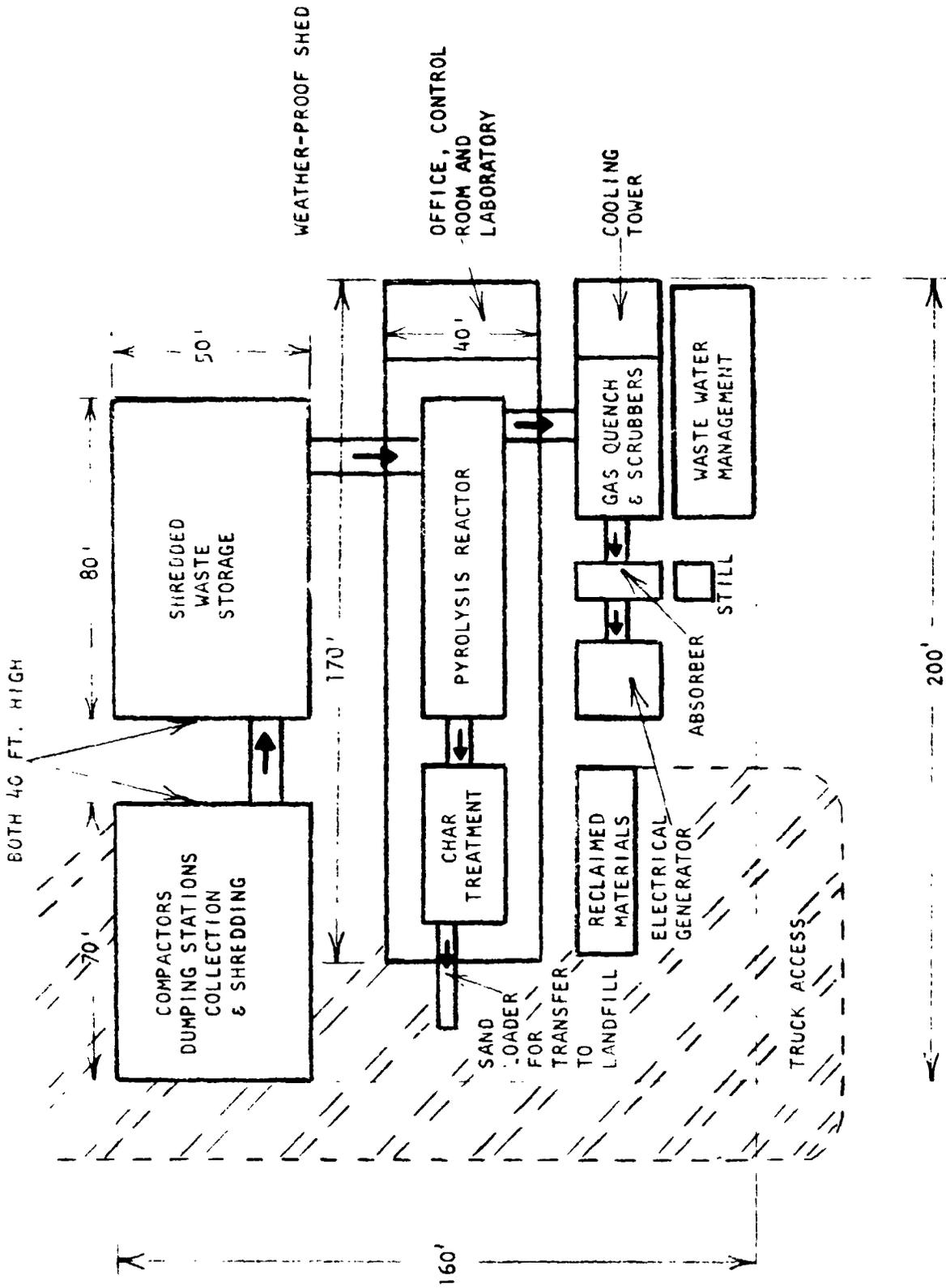


FIGURE 4-1. LAYOUT OF 200-TD MODULE

the scrubber liquor, and the residual ash. The necessary equipment is included in the modular layout to treat these streams to assure compliance with pollution-control standards.

The flue gas from the radiant heaters in the pyrolyser is used to dry the waste before pyrolysis. Flue gases also are exhausted from the electrical generator. These combined gases are vented to the atmosphere through standard gas cleaners.

The scrubber liquor must be treated to reduce its organic content before it can be released from the system. About 75 percent of the organic substances comprising the scrubber liquor are adsorbed by activated carbon. The adsorbed products are principally aromatic substances (entrained and soluble benzene). The remaining substances are amenable to conventional biological treatment. In many areas, the sanitation district probably will accept them for treatment with the municipal sewage. On-site treatment is a feasible alternative. For example, anaerobic upflow filters can be used to convert virtually all of the residual organic matter into methane and carbon dioxide. Gases from anaerobic filters contain 65 to 80 percent methane and are an excellent on-site fuel. Continuous-flow tests have been in progress at RRS for nearly six months on anaerobic treatment of liquors similar to the effluent from the scrubbers.

The residual ash or sands are hauled off to land fill.

4.2 FLOW OF MATERIALS

Figure 4-2 is a flow chart in which the overall process is depicted. The sequence is described in the following paragraphs.

Only minimal sorting is required before pyrolysis. Normal municipal solid waste is shredded into fragments less than 2 inches in any dimension. The shredded waste is fed into a combination feeder-dryer in which it is dried partially, compacted and dropped onto the surface of the molten-lead hearth. See Section 2.1 for a description of the pyrolyser and its action. The purpose of the dryer is described in Appendix B.

The gases from the pyrolyser are quenched and scrubbed of particulate solids by passing them through a water-spray scrubber. Tars and oils also are removed. Considerable water is condensed in the operation; and excess liquor is bled continuously from the circulating load in the scrubber. See Section 4.1 for a discussion of the treatment and disposal of scrubber liquor. Tars, oils and particulate solids are recycled through the pyrolyser.

The cooled gases pass into a light-oil absorber (or alternatively a condenser) in which benzene and related aromatic substances are collected. These constitute a main product of the system. The use of light (petroleum) oils to absorb benzene is standard practice in nearly all coke-oven plants. The pregnant light oils are steam-distilled to recover the aromatics. Condensate, on the other hand, may be marketable directly.

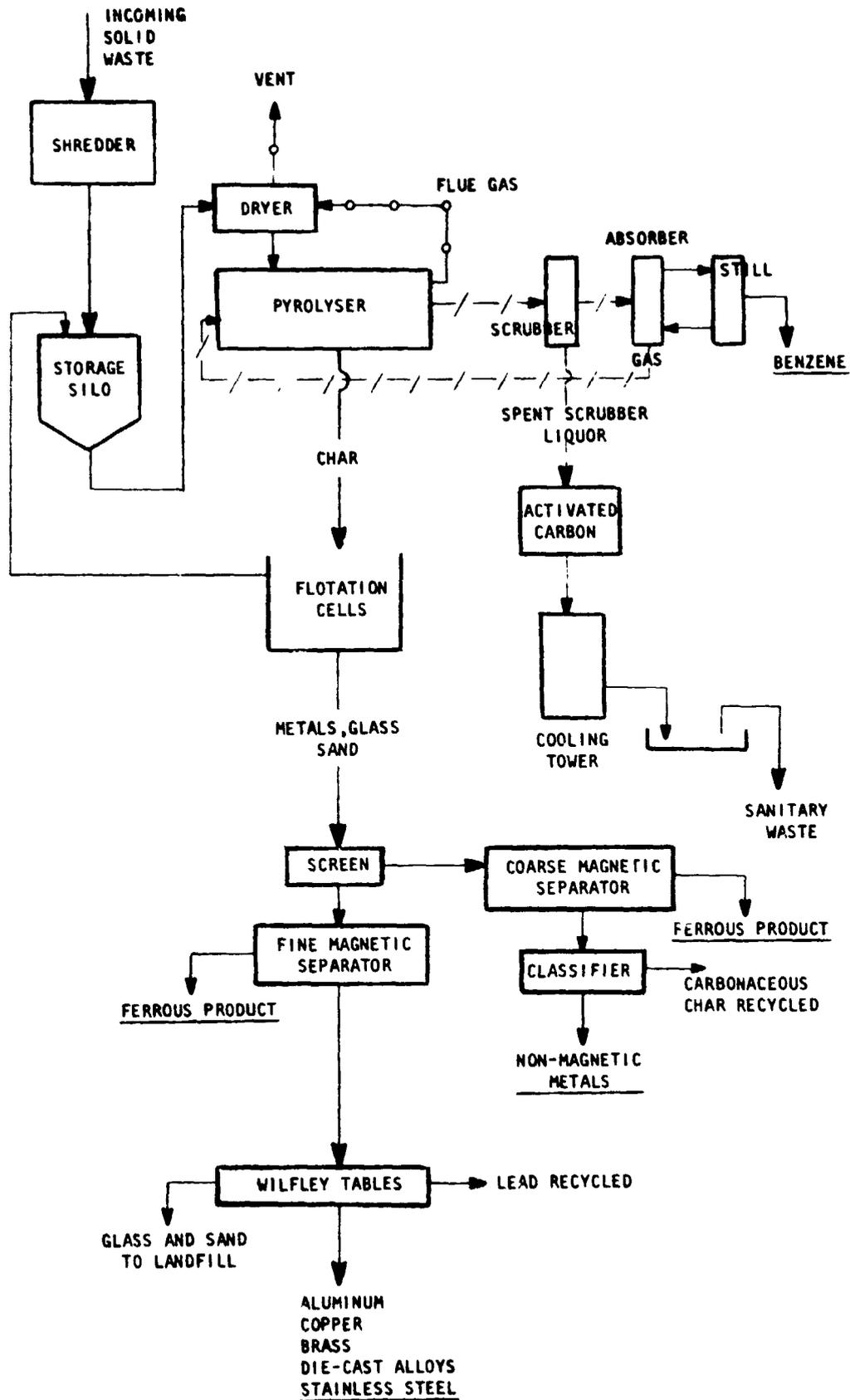


FIGURE 4-2 FLOW CHART, PURETEC® PYROLYSIS SYSTEM

4-4

The fixed gases are dried and burned in the radiant heaters of the pyrolyser as well as in the electrical generator. The reclaimed thermal and electrical energy sustains the system. Any surplus gas is burned elsewhere on site. The system is operated purposely to yield just enough fuel gas to meet on-site requirements. All excess energy is produced in liquid form principally as benzene and toluene. These liquids can be stored conveniently and transported elsewhere at will.

The carbonaceous char is discharged from the pyrolyser intimately mixed with the inert glass, cans and other metals as well as entrained lead. The mixture is blended with a portion of the spent scrubber liquor; and the resulting slurry is subjected to froth flotation. The carbonaceous char is floated from the inert glass and metals. (See Section 2.4.5 in which typical results are cited.) The separated char is recycled through the pyrolyser.

Glass and metals are flushed from the bottoms of the flotation machines and further processed by conventional separation methods. Iron and steel is removed by magnetic methods. Other metals are sorted by gravity concentration. Lead is recovered and recycled through the pyrolyser. Glass is screened from the sands which are discarded to land fill.

4.3 COST EFFECTIVENESS

The tests presented in Section 2 and discussed in Section 3 indicate that the system can be optimized to provide a particularly cost-effective process for waste management. Greatest economies can be achieved by producing just enough gas to sustain the system. Surplus energy is produced in liquid form as aromatic substances principally benzene. These liquids are available as fuel; or, alternatively, they can be sold as chemicals. Nearly complete gasification can be achieved but the surplus gas can not be stored as conveniently as liquids. Much of the gas can be converted to liquid methanol but only at additional expense.

Only minimal presorting and shredding (to 2-inch fragments) are required for lead-bath pyrolysis. Substantial cost savings are a direct result. Electrical power consumption in shredding trash to pieces much less than two inches becomes very costly. Most metals and glass are not affected by the short exposure to molten lead in a reducing atmosphere. Moreover, metal sorting is made easier, because the garbage, paint, grease and plastic insulation coatings are removed in pyrolysis. The burden that must be sorted is reduced by an order of magnitude.

APPENDIX A

MASS BALANCE FOR A TYPICAL HEAT

In this Appendix, a mass balance is presented for Heat 021375, which is typical of tests conducted under NASA (JSC) Contract No. NAS 9-14305. The test was performed under mean conditions. That is to say, it was conducted at 1400 °F. The rate of feed was in the middle of the range investigated as was the moisture content.

The balance is based on proximate analysis of the solid products and analysis of gases by chromatography. Liquids were assayed for chemical oxygen demand (COD). The principal constituents in the tars and oils were identified by infrared spectroscopy.

In addition to the traditional balance--that is, one based on the weights of the various discernible phases--the distribution of the principal chemical elements also is included. Based on few assumptions, a self-consistent accounting can be made of four factors: total weight (of the phases), carbon, hydrogen, and oxygen.

A.1 TEST CONDITIONS

Table A-1 is a summary of the test conditions for Heat 021375.

TABLE A-1

TEST CONDITIONS, HEAT 021375

Temperature, °F	1400
Rate of Feed, lbs/hr waste	27
Retention Time, min	0.9

A.2 TEST DATA

During the course of the test, various weights and measurements were made.

Those pertinent to constructing a mass balance are listed in Table A-2.

TABLE A-2
SUMMARY OF WEIGHTS AND MEASUREMENTS
(Heat 021375)

Total Weight of Feed, lbs	89.84
Total Volume of Gas, scf	517.
Total Increased Weight of Scrubber Liquor, lbs	28.13
Total Weight of Tars and Oils, and Particulate Solids Removed from Scrubber, lbs	2.25

From the data of Table A-2, mean values can be computed for the following:

Rate of Gas Production, scf/lb feed	5.75
Rate of Formation, Tars and Oils (plus Particulate Solids) In Scrubber, lbs/lb feed	.025
Rate of Condensation In Scrubber Liquor, lbs/lb feed	.313

A.3 COMPOSITION OF THE FEED

During Heat 021375, the pyrolyser was fed a blend of the substances listed in Table A-3.

TABLE A-3
SUBSTANCES COMPRISING SIMULATED SOLID WASTE

<u>Component</u>	<u>Weight, lbs/lb feed</u>
Newspaper	0.50
Pine Needles and Bark	.05
Plastics	.03
Water	.24
Inerts (glass, metals)	.18
	<hr/> 1.00

From Table A-3, one can see that 82 percent of the feed is potentially reactive and therefore of major concern. This potentially reactive portion of the waste, in turn, can be viewed as a mixture of water and the four

organic compounds listed in Table A-4.

TABLE A-4
CHEMICAL COMPOUNDS AND ELEMENTS COMPRISING THE POTENTIALLY
REACTIVE PORTION OF THE SIMULATED SOLID WASTE

<u>Chemical Compound</u>	<u>Chemical Element</u>			
	<u>lbs/lb feed</u>	<u>C</u>	<u>H</u>	<u>O</u>
<u>Common Name</u>	<u>lbs/lb feed</u>	<u>C</u>	<u>H</u>	<u>O</u>
Cellulose	0.3077	0.1366	0.0191	0.1520
Hemicellulose	.1190	.0540	.0073	.0577
Lignin	.1233	.0789	.0074	.0370
Polyethylene	.0300	.0257	.0043	--
Water	.2400	--	.0267	.2133
	<u>.8200</u>	<u>0.2952</u>	<u>0.0648</u>	<u>0.4600</u>

The formulation presented in Table A-4 was constructed by assuming that the newspaper was 75% groundwood pulp and 25% chemical pulp. The groundwood pulp and also the pine needles and bark were assumed to be 43% cellulose, 28% hemicellulose and 29 percent lignin. The chemical pulp was assumed to be 100% cellulose. The plastics were essentially polyethylene.

The organic components of the waste are all polymeric substances. That is to say, they are complex giant molecules. Each, however, can be considered as the endless replication of a simple building block, its monomer. Thus cellulose is a polymer of hexosans, where hemicellulose is a polymer of pentosans. Lignin is a polymer of phenylpropane; and polyethylene is formed from ethylene. In Table A-5, the chemical formulas are listed for each polymer with its chemical composition.

TABLE A-5
CHEMICAL COMPOSITION OF THE ORGANIC COMPOUNDS
COMPRISING THE SIMULATED SOLID WASTE

<u>Compound</u>	<u>Formula</u>	<u>Chemical Element, Percent By Weight</u>		
		<u>C</u>	<u>H</u>	<u>O</u>
Cellulose	$(C_6H_{10}O_5)_n$	44.4	6.2	49.4
Hemicellulose	$(C_5H_8O_4)_n$	45.4	6.1	48.5
Lignin	$[C_9H_{8.8}O_{2.4}(OCH_3)]_n$	64	6	30
Polyethylene	$(CH_2 \cdot CH_2)$	85.7	14.3	--

From the formulas listed in Table A-4, the weights of the chemical elements--carbon, hydrogen, and oxygen--can be computed for the potentially reactive portion of the feed. These weights are listed in Table A-4. The percentage distribution is listed in Table A-6.

TABLE A-6
DISTRIBUTION OF CHEMICAL COMPOUNDS AND ELEMENTS
IN THE POTENTIALLY REACTIVE PORTION OF THE SIMULATED SOLID WASTE

<u>Constituent</u>	Pct, Reactive <u>Weight</u>	Distribution by <u>Chemical Element, Pct</u>		
		<u>C</u>	<u>H</u>	<u>O</u>
Cellulose	37.5	46.3	29.5	33.0
Hemicellulose	14.5	18.3	11.3	12.6
Lignin	15.0	26.7	11.4	8.0
Polyethylene	3.7	8.7	6.6	---
Water	29.3	--	41.2	46.4
	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>

A.4 THE COMPOSITION OF THE GASES AND NON-CONDENSED VAPORS

The principal products formed in the pyrolysis of the simulated solid waste were the gases and vapors listed in Table A-7.

TABLE A-7
CHEMICAL COMPOSITION OF GASES AND
NON-CONDENSED VAPORS FROM HEAT 021375

<u>Constituent</u>	<u>By Volume</u>	<u>lbs/lb feed</u>	<u>Percent of the Total Weight of the Potentially Reactive Feed</u>
Hydrogen	16.1	0.0049	0.6
Carbon Monoxide	26.1	.1111	13.4
Methane	21.6	.0526	6.3
Carbon Dioxide	20.4	.1370	16.5
Ethylene	3.2	.0139	1.7
Ethane	0.5	.0022	.3
Benzene	11.3	.1324	15.8
Toluene	0.8	.0109	1.3
	<u>100.0</u>	<u>0.4650</u>	<u>55.9</u>

Nearly 56 percent of the potentially reactive feed was gasified, excluding water. About 17 percent was converted to aromatic substances, principally benzene and toluene.

A.5 COMPOSITION AND QUANTITY OF CHAR

Table A-8 presents the proximate analysis of the char produced in Heat 021375. Proximate analysis is used commonly in the coal industry. It affords a simple means of assessing the quality of a coal for conversion to coke or gases. Most past investigations of solid-waste pyrolysis have used proximate analysis to characterize the char.

TABLE A-8
PROXIMATE ANALYSIS OF CHAR
(Heat 021375)

<u>Component</u>	<u>Percent By Weight</u>
Moisture	1.0
Volatile Matter	2.8
Fixed Carbon	8.8
Ash	<u>87.4</u>
	100.0

The particular sample of char analyzed in Table A-8 assayed 5.6 percent lead. This should not be construed, however, to be representative of lead losses during pyrolysis. Lead was entrained in this char as rather large pieces. Lead had splashed out of the trough and into the discharge shoot. This was caused by a faulty design which later was corrected.

If we assume that the ash of the char is comprised of entrained lead plus the inerts--glass and metal--which were added to the pyrolyser, then the weight of char computes to be:

$$(0.18 \text{ lbs/lb feed}) / (0.874 - 0.056), \text{ or} \\ 0.22 \text{ lbs/lb feed.}$$

In other words, 22 percent of the feed exited from the pyrolyser as residual solids (char). Over 80 percent of the char mass, however, is inert glass and metals. Less than 5 percent of the potentially reactive feed remains as char. Some of the carbonaceous char and ash--about 6 percent of the total weight--exited from the reactor in the gas stream; this is discussed in Section A.6.2.

Samples of the feed also were subjected to proximate analysis. Representative data for two samples are presented in Table A-9.

TABLE A-9

PROXIMATE ANALYSIS OF FEED SAMPLES

	<u>Moisture</u>	<u>Volatile Matter</u>	<u>Fixed Carbon</u>	<u>Ash</u>
Sample A	27.07	49.72	7.12	16.08
Sample B	29.41	49.34	6.20	15.04
Means	28.2	49.5	6.7	15.6
Coefficients of Variation, Pct of Mean	6	0.5	10	5

Proximate analysis reflects the nature of atomic bonding in the pyrolyzed specimen. In the case of relatively volatile (bituminous) coals, the percentage of fixed carbon is nearly equal to the percentage of the so-called aromatic carbon. (See H. C. Howard, "Pyrolytic Reactions of Coal", Chapter 9 in Chemistry of Coal Utilization, Supplementary Volume, H. H. Lowry, Ed., published by John Wiley and Sons, Inc., New York, N. Y., 1963, p. 345). Of the substances comprising the simulated solid waste, only lignin contains aromatic carbon. According to the chemical formula listed in Table A-5, ninety percent of the carbon in lignin occurs as aromatic (covalently bonded) carbon. In other words, 7.1 percent of the feed is aromatic carbon. Note that this is comparable with its fixed-carbon content as recorded in Table A-9.

If we assume that the fixed carbon of the char also is indicative of its lignin content, then the proximate analysis of Table A-8 indicates that the lead-free char is 81.4% ash and 18.6% lignin. This undoubtedly is an oversimplification. The char probably is not simply residual lignin plus inerts. On the other hand, neither is its carbonaceous content pure carbon.

For want of better knowledge let us assume that the relative amounts of carbon, hydrogen and oxygen are the same in the char as in lignin. The assumption fits the experimental facts. Moreover, according to H. W. Eickner (Forest Products Journal, April 1962, pp. 194-199), "once pyrolysis is started, cellulose is volatilized nearly completely and mostly endothermically before 400 °C (752 °F) is reached. Lignin volatilizes more slowly; almost entirely in an exothermic reaction, and loses only one-half of its weight when the pyrolysis is essentially completed at 800 °C (1472 °F)." In other words, there is experimental justification for the assumption that the fixed carbon of our char is aromatic carbon derived from the lignin of the solid waste. Lignin contains about 57 percent aromatic carbon; and, therefore, if its char is equal to one-half its initial weight, then the char is essentially pure carbon.

A.6 SCRUBBER PRODUCTS

During the scrubbing of the hot gases from the pyrolyser, a significant

quantity of water is condensed. Oils and tars also are removed with particulate solids.

A.6.1 CONDENSED LIQUOR

Examination of the liquor indicates that it contains entrained benzene and toluene. It also contains water-soluble acetic acid and some ammonia. Viewed overall, however, the liquor is essentially water. Its COD increased from 300 to 600 mg/l O. This indicates that the total water-soluble and entrained organic substances including aromatics are less than 0.0001-0.0002 lbs/lb feed.

A.6.2 TARS, OILS AND PARTICULATE SOLIDS

About 2-1/4 pounds of solids were removed from the scrubber at the conclusion of the test (Heat 021375). These oil-soaked solids were extracted with chloroform; and the residue subjected to proximate analysis. The chloroform extract was analyzed by infrared spectroscopy. From these analyses, it was concluded that the scrubber solids were comprised of the following three classes of substances:

Tars and oils, principally naphthalene	45 percent
Carbonaceous char	45 percent
Fly ash	10 percent

In Heat 021375, the total weight of scrubber-solids amounted to 0.025 lbs/lb feed.

Particulate debris is swept from the pyrolyser in the gas stream. These gas-borne solids act as a bed for condensing oils and tars which polymerize from aromatic vapors. As was discussed previously in Section A.5, the gas-borne debris--carbonaceous char plus fly ash--amounts to about six percent of the total weight of char (carbonaceous residue plus inert glass and metals). About 28 percent of the total carbonaceous residue and 2 percent of the inert ash are blown from the pyrolyser in the gas stream.

A.7 ACCOUNTABILITY

A summary of the products is presented in Table A-10, which lists the total weight of the substances and of the chemical elements comprising them. Accountability as indicated in the table is excellent. In preparing Table A-10, the total weight of ash was taken as 0.18 lbs/lb feed--the known rate at which glass and metal were added to the pyrolyser. Ash exited from the system as fly ash and as ash in the main char stream. Residual carbonaceous debris likewise exited in the gas stream and in the main char stream. In constructing Table A-10, the weights of ash and carbonaceous residue were divided between these two streams to reflect the relative weights of each in the two streams as determined experimentally.

TABLE A-10
 SUMMARY OF PRODUCT YIELD BY WEIGHT
 (Heat 021375)

Compound	Substances Comprising Products of Pyrolysis lbs/lb feed	Chemical Elements lbs/lb feed		
		C	H	O
Gases				
Hydrogen	0.0049	--	0.0049	--
Carbon Monoxide	.1111	0.0476	--	0.0635
Methane	.0526	.0394	.0132	--
Carbon Dioxide	.1370	.0374	--	.0996
Ethylene	.0139	.0119	.0020	--
Ethane	.0022	.0018	.0004	--
Benzene	.1324	.1222	.0102	--
Toluene	.0109	.0100	.0009	--
Char				
Carbonaceous Portion (as lignin)	0.0288	0.0184	0.0017	0.0086
Ash	.1775	--	--	--
Water	.3131	--	0.0348	0.2783
Scrubber Solids				
Particulate Char (as lignin)	0.0113	0.0072	0.0007	0.0034
Fly ash	.0025	--	--	--
Tars and Oils (as naphthalene)	.0113	0.0107	0.0006	--
TOTAL WEIGHT	1.0095	0.3066	0.0694	0.4534
ACCOUNTABILITY	101%	104%	107%	99%

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A.8 DISTRIBUTION OF WEIGHT AMONG THE PRODUCTS

Table A-11 presents a summary of the products and the percentage of the total feed weight each represents. Gases amount to 46 percent of the total; and water is 31 percent. Thus 77 percent of the feed was gasified. Of the remaining 23 percent, inert glass and metals account for nearly eighty percent. Residual carbonaceous solids represent only 4 percent of the feed.

TABLE A-11
DISTRIBUTION OF WEIGHT AMONG PRODUCTS

	<u>Percentage of Weight of Feed</u>	
Gases		46.0
Hydrogen	0.5	
Carbon Monoxide	11.0	
Methane	5.2	
Carbon Dioxide	13.6	
Ethylene	1.4	
Ethane	.2	
Benzene	13.1	
Toluene	1.0	
Char		20.5
Carbonaceous Portion	2.8	
Ash	17.7	
Water	31.0	31.0
Scrubber Solids		2.5
Particulate Char	1.1	
Fly Ash	.3	
Tars and Oils	1.1	
	<u>100.0</u>	<u>100.0</u>

A.9 EVALUATION TREATING MOISTURE AS AN INERT

Water was probably not a reactant in this test. More water was removed from the system than added. Let us assume that moisture plays no role in the chemical reactions contributing to pyrolysis. Then the actually reactive feed is substantially less than the potentially reactive feed used as an evaluator in previous sections; and the product yield should be re-evaluated in terms of dry organic mass.

Table A-12 is a summary of the products in which the percentage distribution is presented in terms of the actually reactive feed, i.e., the dry organic mass. Compare the distribution presented at the bottom of Table A-12 for the feed constituents with that presented in Table A-6. Treating moisture as an inert significantly alters the distribution of hydrogen and

oxygen. Excluding water, cellulose is the prime source of both. The related hemicellulose is the second source. These are also the principal sources of carbon.

TABLE A-12

DISTRIBUTION OF WEIGHT AND CHEMICAL ELEMENTS
AMONG THE ACTUALLY REACTIVE PORTION OF HEAT 021375

<u>Product</u>	Percentage of Reactive Feed (By Weight)			
	<u>Total Weight</u>	<u>Carbon</u>	<u>Hydrogen</u>	<u>Oxygen</u>
Hydrogen	0.8	--	11.5	--
Carbon Monoxide	18.8	15.5	--	26.4
Methane	8.9	12.9	30.9	--
Carbon Dioxide	23.2	12.2	--	41.5
Ethylene	2.4	3.9	4.7	--
Ethane	.4	.6	.9	--
Benzene	22.5	39.8	23.9	--
Toluene	1.8	3.3	2.1	--
Carbonaceous Char (including gas-borne debris)	6.8	8.3	5.6	5.0
Chemically Formed Water	12.5	--	19.0	27.1
Tars and Oils	<u>1.9</u>	<u>3.5</u>	<u>1.4</u>	<u>--</u>
	100.0	100.0	100.0	100.0
 <u>Feed Constituent</u>				
Cellulose	53.0	46.3	50.1	61.6
Hemicellulose	20.5	18.3	19.2	23.4
Lignin	21.3	26.7	19.4	15.0
Polyethylene	<u>5.2</u>	<u>8.7</u>	<u>11.3</u>	<u>--</u>
	100.0	100.0	100.0	100.0

About 24 percent of the reactive feed carbon is aromatic, but in the products about 42 percent of the carbon is aromatic. Substantial aromatization has occurred.

About two thirds of the oxygen contained in hemicellulose and one half of that in cellulose exist in hydroxyl groupings; and the remainder is bonded to carbon. In the products, however, two thirds of the oxygen appears as carbonaceous gases (CO and CO₂); the remainder is in water.

APPENDIX B

CALCULATION OF SYSTEM EFFICIENCY

Pyrolysis has the potential of generating surplus energy. That is to say, the calorific value of the products exceeds the energy required to sustain the system. The development of pyrolysis systems generally is monitored by so-called systems-efficiency factors. These factors indicate the percentage of the input energy available for use outside of the system. In this Appendix, methods are outlined for computation of the systems efficiency (SE) as defined by NASA (JSC) for use in this contract. Values of SE including the minimum are calculated for ramifications of the basic system.

B.1 DEFINITION

For the purposes of this contract, system efficiency (SE) is defined as follows:

$$SE = (Q_p - Q_s)/Q_f, \quad (B-1)$$

in which Q_p is the useful energy that can be derived from the products;

Q_s is the energy required to operate the system; and

Q_f is the useful energy available in the feed.

In following sections, each of the terms comprising Equation B-1 is defined; and mean values of each are computed for the PURETEC[®] system.

B.2 USEFUL ENERGY AVAILABLE IN THE FEED

Table B-1 summarizes the energy content of the baseline feed used in this program. The so-called high heating value (HHV) of the waste is 5220 Btu/lb feed, whereas its low heating value (LHV) is 4987 Btu/lb. In computing the system efficiency (SE), established convention was followed; and the high heating value was used. Consequently, a lower SE is reported than that obtainable from the LHV.

TABLE B-1

ENERGY CONTENT OF SIMULATED SOLID WASTE

<u>Component</u>	<u>Percent By Weight</u>	<u>Contribution To Energy Content, Btu/lb feed</u>
Moisture	24	-233*
Organic Substances (mostly newspaper)	58	5220**
Inerts	<u>18</u>	<u> </u>
	100	4987

* Assuming the latent heat of vaporization is 970 Btu/lb H₂O.

** Assuming the heat of combustion is 9000 Btu/lb dry organic solids.

B.3 ENERGY REQUIRED TO OPERATE THE SYSTEM

To sustain pyrolysis sufficient heat must be added to the system to replace the heat lost from the system. In addition some mechanical energy is required to operate the transport mechanism and the ancillary grinding and sorting equipment. (Generally this is supplied as electricity.) Expressed mathematically, q_s , the energy required to sustain the system, is the sum of the terms on the right-hand side of the following equation:

$$q_s = q_l + q_f + q_v + q_r + q_e \quad (B-2)$$

The term q is related to Q_c , the energy required to operate the system, by a factor whose magnitude reflects the efficiency of burning fuel gas in the radiant heaters. This is discussed further in the later section B.3.6.

In Equation B-2, the symbols have the following significance:

- q_l heat lost from the system by conduction, convection, and radiation
- q_f sensible heat supplied to the feed; specifically, the sensible heat of the dry organic and inert substances
- q_v heat consumed in evaporating water from moist feed
- q_r heat consumed in chemical reactions
- q_e energy converted to electricity to operate various machinery

Each of these terms is defined further in the following subsections. Representative values are cited for the RRS PURETEC[®] Pyrolysis System.

B.3.1 INSULATION LOSSES

Energy is dissipated continuously from the system by natural conduction, convection and radiation to the ambient. The furnace proper is insulated by thermal protecting materials to minimize these losses. For convenience, these losses, q_l , can be expressed in terms of the weight of feed added to the system.

For example, a full-scale unit probably must treat 200 tons daily of municipal solid waste. The furnace proper would be about 25 feet long, 80 feet width and 7-1/2 feet high. Its insulation will be 13-1/2 inch firebrick. Losses from the unit will not exceed 1.67 million Btu/hr. In other words,

$$q_l = 100 \text{ Btu/lb feed}$$

B.3.2 SENSIBLE HEAT OF THE FEED

Presently, cold feed is added directly to the pilot-plant pyrolyser. Thus energy is consumed continuously in heating the feed to the operating

temperature of the reactor. Two of the three components comprising the sensible heat of the feed are discussed in subsections. The third-- steam--is discussed in the following section.

a. Energy Consumed In Heating Organic Substances.

The specific heat of the organic substances in the solid waste is assumed to be 0.3 Btu/lb. Therefore, q_o , the sensible heat requirement is as follows:

$$\begin{aligned}q_o &= \text{mass} \times \text{specific heat} \times \Delta T \\&= 0.58 \times 0.30 \times (1400 - 70) \\&= 230 \text{ Btu/lb feed.}\end{aligned}$$

b. Energy Consumed In Heating Inert Constituents.

The specific heat of the inert glass and metals is taken to be 0.2 Btu/lb. Hence, q_i , the sensible heat requirement is as follows:

$$\begin{aligned}q_i &= 0.18 \times 0.2 \times (1400 - 70) \\&= 50 \text{ Btu/lb feed.}\end{aligned}$$

B.3.3 ENERGY CONSUMED IN EVAPORATING MOISTURE

The evaporation of water to steam is the greatest single expenditure of energy in pyrolysis. Assuming that water at 70 °F is evaporated and superheated to 1400 °F,

$$\begin{aligned}q_v &= 0.24 \times (1745 - 38) \\&= 410 \text{ Btu/lb feed.}\end{aligned}$$

B.3.4 ENERGY CONSUMED IN THERMAL DECOMPOSITION OF THE ORGANIC COMPOUNDS

The pyrolysis of cellulose, the principal organic constituent in the waste, is endothermic. The energy consumed in the thermal decomposition of solid waste has been estimated to be 700 Btu/lb organic solids. (See G. M. Mallan and C. S. Finney, "New Techniques in the Pyrolysis of Solid Wastes", AIChE Symposium Series, Vol. 69, No. 133, 1973, p 59.) Using this value,

$$\begin{aligned}q_r &= 0.58 \times 700 \\&= 405 \text{ Btu/lb feed}\end{aligned}$$

B.3.5 ELECTRICAL ENERGY REQUIRED TO OPERATE THE SYSTEM

The largest single expenditure of electricity is the power consumption in shredding the solid waste. According to Mallan and Finney (Op Cit.), the shredding of solid waste to less than 2-inch fragments requires about

45 hp hrs per ton (57.25 Btu/lb). If electricity is generated on site from pyrolysis gas, the efficiency of the conversion probably will be about 20 percent. Consequently, gas equivalent to 285 Btu will be consumed in shredding one pound of feed. For design purposes, let

$$q_e = 300 \text{ Btu/lb feed.}$$

B.3.6 CALORIFIC VALUE OF THE FUEL GAS REQUIRED TO SUSTAIN PYROLYSIS

The energy to sustain the system, Q_s , in practice, is obtained by burning a portion of the gases produced in pyrolysis. This is done in the radiant heaters in the roof of the furnace. Let us assume a 50% efficiency in this heating process. Then,

$$\begin{aligned} Q_s &= 2(q_l + q_f + q_v + q_r) + q_e \\ &= 2(1195) + 300 \\ &= 2690 \text{ Btu/lb feed.} \end{aligned}$$

B.4 ENERGY CONTENT OF THE PRODUCTS

Excluding water and carbon dioxide, the products of pyrolysis are combustible substances. Table 3-5, which appears in Section 3 of the main report lists the energy content of the gases and vapors formed from ten pilot-plant tests, (on feed containing 24-pct moisture). These tests were performed over a range of conditions. The mean value for the calorific content of the gases is 2732 Btu/lb. The vapors--benzene and toluene--have a potential fuel value of 2082 Btu/lb feed, according to the mean of the ten tests listed in Table 3-5, Section 3.

In addition to the gases and vapors, the char, tars and oils are potential fuels. According to the mass balance presented in Appendix A, the organic content of these minor products is equivalent to 0.05 lbs/lb feed. Assuming a mean heat of combustion of 10,000 Btu/lb organic solids, the useful energy available in the char, tars and oils is as follows:

$$0.05 \times 10,000 = 500 \text{ Btu/lb feed.}$$

The total useful energy available in the products is the sum of that contained in the gases, vapors and the carbonaceous residual solids. In other words,

$$\begin{aligned} Q_p &= 2732 + 2082 + 500 \\ &\approx 5315 \text{ Btu/lb feed.} \end{aligned}$$

B.5 MINIMUM SYSTEM EFFICIENCY

If all of the products are utilized as fuel, the system efficiency is as follows:

$$\begin{aligned}
 SE &= (Q_p - Q_s)/Q_f \\
 &= (5315 - 2690)/5220 \\
 &\approx 0.50
 \end{aligned}$$

In other words, the system is 50 percent efficient. That is to say, only 50 percent of the produced energy is needed to sustain the process. The remaining 50 percent is available for use outside of the system.

Note that the calorific value of the gases alone--excluding the vapors, benzene and toluene--is more than sufficient to sustain the system: the mean value of the gases is 2732 Btu/lb; and the energy required to sustain the system is 2690 Btu/lb.

B.6 OPTIMUM SYSTEM EFFICIENCY

Improved performance can be achieved by utilizing the sensible heat of the flue gases to evaporate a portion of the moisture. For example, suppose that the flue gases are exhausted from the radiant heaters through a duct surrounding the exterior of the feed chute. Arranged in this manner, the feeder also serves as a tunnel dryer. Steam forms in the feeder and enters the pyrolyser with the waste, where it is utilized to flush the gases and vapors from the pyrolyzing waste. Let us examine the efficiency of this system:

(1) According to the Fifth Edition of Perry's The Chemical Engineers' Handbook (page 20-24), the thermal efficiency of a dryer will vary from 20 to 50 percent. Let us assume that 33 percent efficiency can be achieved in our tunnel dryer and that the temperature of the waste is 225 °F as it exits from the dryer.

(2) If M is the moisture remaining in the waste after it has passed through the feeder-dryer, then the energy supplied to the dryer can be expressed, in Btu/lb feed, as follows:

a. Supplied To Remaining Moisture

$$M[(h_g)_{212} - (h_g)_{70}] = (180 - 38)M = 142M$$

b. Expended in Evaporation

$$\begin{aligned}
 (0.24 - M)[(h_v)_{225} - (h_g)_{70}] &= (0.24 - M)(1155 - 38) \\
 &= 268 - 1117M
 \end{aligned}$$

c. Supplied to Organic Substances

$$0.58 \times 0.3 \times (225 - 70) = 27$$

d. Supplied to Inert Substances

$$0.18 \times 0.2 \times (225 - 70) = 6$$

c. Total Energy Supplied to the Dryer (Sum of a,b,c and d)

$$301 - 975M$$

(3) The radiant heaters must supply the following energy (in Btu/lb feed):

a. The Heat Lost by Conduction, Convection and Radiation from the System

$$100$$

b. Energy Required to Evaporate Remaining Moisture

$$M[(h_v)_{1400} - (h_g)_{212}] = M(1745 - 180) = 1565M$$

c. Energy to Superheat Incoming Steam

$$(0.24 - M)[(h_v)_{1400} - (h_v)_{225}] = (0.24 - M)(1745 - 1155) \\ = 142 - 590M$$

d. Energy to Heat Organic Substances

$$0.58 \times 0.3 \times (1400 - 225) = 204$$

e. Energy to Heat Inert Substances

$$0.18 \times 0.2 \times (1400 - 225) = 42$$

f. Total Energy Supplied by Radiant Heaters (Sum of a,b,c,d and e)

$$488 + 975M$$

(4) As the radiant heaters have a thermal efficiency of 50 percent, the energy content of the flue gases is equal to the energy supplied to the system by the radiant heaters. Therefore, the energy balance for the dryer can be expressed by the following equations:

$$0.33(488 + 975M) = 301 - 975M$$

$$161 + 322M = 301 - 975M$$

(5) Solving the equation,

$$M = 140/1297 = 0.11$$

In other words, 54 percent of the moisture is evaporated in the feeder by energy supplied from the flue gases.

(6) Assuming that the fuel value of the products is the same as in the previous example (cf. Section B.5), the system efficiency is as follows:

$$\begin{aligned} SE &= \frac{5315 - 2(488 + 975M) - 300 - 100}{5220} \\ &= (5315 - 1190 - 300 - 100)/5220 \\ &= 3725/5220 \\ &= 0.71 \end{aligned}$$

By utilizing the sensible heat of the flue gases, the system efficiency has been increased to over 70 percent.

In the foregoing calculations, the symbol h denotes the enthalpy of water in Btu per lb. The subscripts l and v designate the liquid and vapor phases, respectively. The temperature of the phase, in degrees Fahrenheit, also is indicated by a subscript. Values for the enthalpy were taken from H. Keenan and F. G. Keyes, Thermodynamic Properties of Steam, First Edition, John Wiley & Sons, Inc., New York, 1936, 89 pp.